

IX. *The Absorption Spectra of the Alkaloids.*

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Received November 19, 1884, and March 5, 1885.*—Read December 11, 1884, and March 12, 1885.

[PLATES 53–56.]

CONTENTS.

	Page
Introduction	471
Experimental details	472
Method of determining the wave-lengths of absorption spectra	473
Index to the solutions examined	477
The measurements and descriptions of spectra	479
Summary	513
Conclusions	520

Introduction.

MANY of the poisonous alkaloids give no distinctive chemical reactions by which they can be identified, and in certain cases the means of recognising them are restricted to observations on their crystalline form and physiological action. Some of the alkaloids have never been crystallised, and even such as are usually obtained in crystals are not always recognisable, because their shape is not invariably a well-marked or characteristic feature; moreover the form and grouping of crystals is occasionally modified by such reactions or treatment as may be necessary in the extraction of an organic base. Small admixtures of foreign substances also modify crystalline character, and not infrequently cause a crystalline substance to become amorphous. No absolute reliance

* This communication was presented to the Society in two parts. The information concerning aconitine, pseudaconitine, japaconitine, morphine, narcotine, codeïne, thebaine, papaverine, oxynarcotine, apomorphine hydrochloride, cotarnine hydrobromide, tetracetyl morphine, diacetyl codeïne, quinine, quinine sulphate, cinchonine sulphate, quinidine sulphate, cinchonidine sulphate, veratrine, piperine, brucine, strychnine, narceïne, aconitine (foreign), cevadine, atropine, solanine, hyoscyamine, digitaline, picrotoxine, nicotine, and caffèïne formed Part I. (Received November 19, 1884. Abstract published in Proc. Roy. Soc., vol. xxviii., p. 1.) That concerning pyridine, piperidine, quinoline, tetrahydroquinoline, quinoline hydrochloride, and the specimens of aconitine received from Dr. STEVENSON formed Part II. (Received March 5, 1885. Abstract published in Proc. Roy. Soc., vol. xxviii., p. 191.)

can be placed upon the mere appearance of crystals; they must be submitted to recrystallisation by sublimation or some other process. The physiological action of certain alkaloids of an extremely deadly character is remarkable enough to prove a means of identifying the substance when the effect on the human subject is under observation; but it is to some extent capable of being modified by the extent of the dose, the administration of other drugs, or the idiosyncrasy of the patient. These facts are well known, and are generally made use of by the counsel for the defence in medico-legal cases. When the identification of an alkaloid is a necessary part of the evidence of the administration of poison, experiments of a physiological character have necessarily to be made on the lower animals. It has been objected that the action of drugs on creatures of a smaller size and different organisation may be, and, in certain cases, indeed is, unlike that produced in the human organism, and comparative experiments are necessary in which the suspected substance is compared with authentic specimens before its identity can be established. But in such comparative experiments an element of uncertainty is introduced, because various preparations supposed to be the same alkaloid may differ in physiological action to such an extent that reasonable doubts may be entertained as to whether they consist of the same substance or, indeed, of one substance only. The whole subject of the modification of alkaloids by the reagents used in their extraction, variations in their crystalline character and in their physiological action, can be well illustrated by reference to the researches of Dr. C. R. A. WRIGHT on the various preparations known as aconitine.

The evidence given at the trial of GEORGE HENRY LAMSON, a surgeon, at the Central Criminal Court in 1882, for poisoning with aconitine, conferred greatly increased importance upon any method of absolute physical measurement which might be substituted for the ordinary tests in the identification of the dangerous alkaloids. Almost all active alkaloids have a complex chemical constitution, and every complex molecule in which carbon is in a certain state of condensation has a definite absorption spectrum in the ultra-violet if not in the visible region. In most cases the absorption curve is peculiar and often strikingly characteristic, and only minute quantities of material are actually required for obtaining measurements of spectra from which such curves may be plotted. The interest that attaches to an examination of the absorption spectra of the alkaloids is not alone the fact that a means of recognising, detecting, and estimating, such substances may be devised, but still more that we may learn something of their chemical constitution.

The experimental details.

The method of examination employed was that described in the Phil. Trans., Vol. 170, p. 257, 1879, but the spectroscope was the short focussed instrument employed for photographing the spectra published in the 'Journal of the Chemical Society,' vol. xli., p. 84.

Several modifications were introduced with the object of gaining accuracy and reducing the amount of labour entailed by a large series of observations.

1st. The solutions were as far as possible made up to the same strength, and cells of definite thickness were employed in series as 5 millims., 4 millims., 3 millims., 2 millims., and 1 millim. This obviated the necessity for repeatedly diluting the solutions, and so greatly facilitated the work; while it diminished the possibility of errors, especially in the descriptions of the spectra.

2nd. The measurements were all reduced to wave-lengths, and the absorption curves were plotted accordingly. As the curves have been made continuous the necessity for shading has been avoided.

3rd. While the absorption curves serve for the comparison of one alkaloid with another, as a ready means of distinguishing them and of estimating the quantity present in a solution, a very careful description of the spectra from which the curves were drawn has been furnished, so that no essential details have been omitted such as were found to be imperfectly represented by the drawings.

4th. The rays intended to give a suitable spectrum were obtained from metallic points, which, for the purpose, are superior to all others. In previous researches, electrodes of cadmium or of nickel alloyed with a small quantity of copper, in certain cases metallic indium and iron have been used. None of these are quite satisfactory. The cadmium and indium lines are not sufficiently close together or numerous, the wave-lengths of the iron and nickel lines had not been determined when these experiments were in progress; moreover, they were deemed unsuitable because there is too great a difference between the intensity of the lines in different parts of the spectrum, so that deceptive results are obtained when feeble absorptions occur.

The electrodes I prefer to all others are cadmium, tin, and lead; the lines of tin and lead are numerous and well distributed throughout the whole spectrum; they are distinctive in character, and therefore easily recognisable, which is not the case with the iron and nickel lines. The cadmium lines preponderate in intensity, but the emissive power of the cadmium is purposely reduced by diminishing the quantity of that metal in the spark.

Thus I take for one electrode an alloy of tin with 25 per cent. of cadmium, for the other an alloy of lead with the same proportion of cadmium. When the two are used as opposite electrodes a spark spectrum is obtained every line in which can be easily recognised; the tin lines are on one side, and stretch half-way across; the lead are on the other side; while the cadmium contained in both electrodes causes the lines of that metal to stretch across from point to point. A somewhat longer exposure than usual fills the intervals between the lines with a weaker continuous spectrum. The period was three minutes. The extent of the continuous rays is always noted in the descriptions of the absorption spectra. To secure well-defined spectra the photographs were taken with the solutions placed in front of the slit, and the rays were concentrated by a condensing lens of two inches diameter and three inches focal length.

Method of determining the wave-lengths.

It was usual to take a series of five or six photographs of each solution on one plate, and thus the spectra represent the rays transmitted by 1, 2, 3, 4, 5, or more millimetres of the absorbent liquid. The wave-lengths referred to are derived from those given in the Phil. Trans., Vol. 175, p. 63, 1884, for cadmium, tin, and lead. The scale numbers in hundredths of an inch are arbitrary, and quite different from those given beside the wave-lengths in the paper quoted; they were actually read off from photographs of the electrodes by means of an ivory scale, the end of which coincided with the end of the glass plate. The scale originally used was a photograph of the spectrum of the electrodes with divisions etched on the glass, the gelatine film being scraped off just below the lines to admit of the glass being etched. The divisions were hundredths of an inch, and every fifth line was distinguished by the corresponding wave-length being written on the back of the plate opposite to the longer line. The figures, however, are too small, and, otherwise, from the transparency of the glass difficult to read when applied to the face of another photograph. It was found more satisfactory to apply an ivory scale with a bevelled edge, divided as aforesaid, so that the scale numbers arbitrarily fixed first for the cadmium lines are read off on all the other lines. The scale is held in position by a pair of wooden spring clips. Supposing an absorption band occurs near the line 120 ($\lambda=3245.5$), then 120 on the scale is brought over this line on the photograph; if it be seen to extend to 240 or thereabouts ($\lambda=2593$), the reading on the scale is brought up to this line, and a more exact measurement is made. If the adjustment is not further from the correct number than $\frac{1}{100}$ th of an inch, it is sometimes not worth while to alter it; but whenever it is necessary to make accurate measurements, the scale is capable of easy and perfect adjustment to any part of the spectrum. For the purpose of converting the scale measurements into wave-lengths and their reciprocals, two curves have been drawn on one sheet of paper. The scale numbers, wave-lengths, and oscillation frequencies of the fiducial lines employed for the interpolation curves are stated on p. 475. Fractions of a tenth-metre have been omitted as being unnecessary in dealing with absorption spectra.

On the diagrams the scale of wave-lengths is reduced to millionths of a millimetre.

LINES of cadmium, tin, and lead used for the interpolation curve.

Scale-numbers.		λ .	$\frac{1}{\lambda}$.	Scale-numbers.		λ .	$\frac{1}{\lambda}$.
Hundredths of an inch.				Hundredths of an inch.			
0	190.0	Sn	2812	3556
4.5	192.5	Pb	2801	3571
20.5	Cd (7)	4414	2265	197.0	Sn	2778	3599
22.5	Pb	4386	2280	203.5	Cd (17)	2747	3640
30.5	Pb	4245	2355	213.0	Sn	2705	3696
42.75	Pb	4061	2462	223.0	Pb	2662	3756
	Air	3994		235.0	Pb	2613	3827
62.0	Sn	3800	2503	240.0	Sn	2593	3856
67.3	Pb	3739	2674	244.0	Pb	2576	3882
72.0	Pb	3683	2715	245.0	Cd (18)	2572	3888
76.3	Pb	3639	2748	245.5	Sn	2570	3891
79.0	Cd (9)	3610	2770	247.0	Pb	2561	3904
82.7	Pb	3572	2799	252.5	Sn	2545	3929
93.7	Cd (10)	3465	2886	266.5	Sn	2495	4008
97.0	Air	3437	2910	270.0	Sn	2483	4027
101.0	Cd (11)	3403	2938	272.0	Pb	2475	4040
106.5	Sn	3352	2983	281.3	Pb	2445	4090
109.5	Sn	3330	3003	282.0	Pb	2442	4095
115.0	Sn	3283	3045	286.5	Sn	2429	4116
118.0	Sn	3262	3065	289.0	Sn	2422	4128
119.5	Cd (12)	3260	3067	295.0	Pb	2402	4163
129.5	Sn	3174	3150	298.0	Pb	2393	4178
135.0	Pb	3137	3187	306.0	Sn	2368	4223
151.0	Sn	3033	3297	311.0	Sn	2355	4246
155.0	Sn	3008	3324	318.0	Sn	2335	4282
159.5	Cd	2980	3355	320.0	Cd	2329	4293
165.0	Pb	2949	3391	322.7	Cd	2321	4308
171.0	Sn	2912	3434	325.7	Cd (23)	2313	4323
177.0	Cd	2880	3472	335.0	Cd & Sn	2288	4370
178.5	Pb	2872	3481	344.0	Cd (24)	2265	4415
180.0	Sn	2862	3494	351.0	Sn	2247	4450
182.5	Sn	2849	3510	353.5	Cd	2241	4462
185.0	Sn	2839	3524	368.5	Pb	2205	4535
186.0	Pb	2832	3531	372.5	Cd	2195	4555
188.0	Pb	2822	3543	395.0	Cd	2145	4662

In this research the wave-length numbers have alone been quoted. The mode of proceeding after a series of photographs had been taken was, after measuring, to record and reduce the measurements to wave-lengths. The numbers obtained were then laid down on suitably ruled paper for the absorption curve to be plotted. It was then generally found necessary to execute a further series of photographs, and sometimes two or three series of the absorptions caused by more dilute or stronger solutions, in order to obtain the maximum and minimum effect of the absorbent substance as well as the coefficients of absorption for all intermediate wave-lengths. The curves drawn are continuous, so that the necessity for shading is obviated; the unshaded diagrams are not such true representations of the photographs, but these less exact diagrams are supplemented by very careful and accurate descriptions. Authentic

specimens of alkaloids and other substances in a state of great purity were for the most part obtained from the chemists by whom they were prepared, namely, Messrs. T. and H. SMITH and SON, of Edinburgh, Dr. C. R. A. WRIGHT, and Mr. DAVID HOWARD. I am particularly indebted to Dr. STEVENSON and Dr. C. R. A. WRIGHT for several aconitine specimens, also to Mr. DAVID HOWARD for the cinchona alkaloids.

The substances examined were the following :—

ALKALOIDS of the Aconites.

Aconitine from <i>A. Napellus</i>	$C_{33}H_{49}NO_{12}$
Pseudaconitine from <i>A. Ferox</i>	$C_{36}H_{43}NO_{12}$
Japaconitine from a species of Japanese aconite . .	$C_{66}H_{88}N_2O_{21}$
Aconitine from a foreign source ; probably picraconitine.	

ALKALOIDS of the Cinchonas.

Cinchonine	$C_{20}H_{24}N_2O$
Cinchonidine sulphate	$(C_{20}H_{24}N_2O)_2 \cdot H_2SO_4 \cdot 2Aq$
Quinine	$C_{20}H_{24}N_2O_2$
Quinine sulphate	$(C_{20}H_{24}N_2O_2)_2 \cdot H_2SO_4 \cdot 2Aq$
Quinidine sulphate	$(C_{20}H_{24}N_2O_2)_2 \cdot H_2SO_4 \cdot 2Aq$

ALKALOIDS of the Papaveraceæ.

Morphine	$C_{34}H_{38}N_2O_6$
Codeïne	$C_{36}H_{42}N_2O_6$
Narcotine	$C_{22}H_{23}NO_7$
Narceïne	$C_{23}H_{29}NO_9$
Papaverine	$C_{21}H_{21}NO_4$
Thebaine	$C_{19}H_{21}NO_3$

DERIVATIVES of the Opium bases.

Tetracetyl-morphine	$C_{34}H_{34}(C_2H_3O)_4N_2O_6$
Diacetyl-codeïne	$C_{36}H_{40}(C_2H_3O)_2N_2O_6$
Oxynarcotine	$C_{22}H_{23}NO_8$
Cotarnine hydrobromide	$C_{12}H_{13}NO_3 \cdot HBr$
Apomorphine hydrochloride	$C_{17}H_{17}NO_2 \cdot HCl$

ALKALOIDS of the Solanaceæ.

Nicotine	$C_{10}H_{14}N_2$
Solanine	$C_{42}H_{87}NO_{15}$
Atropine	$C_{17}H_{23}NO_3$

ALKALOIDS of Strychnos.

Brucine	$C_{23}H_{26}N_2O_4 \cdot 4H_2O$
Strychnine	$C_{21}H_{22}N_2O_2$

ALKALOIDS of Veratrum.

Veratrine	$C_{37}H_{53}NO_{11}$ (COUERBE'S Veratrine)
Cevadine	$C_{32}H_{49}NO_9$ (MERCK'S Veratrine)

VARIOUS other Alkaloids.

Digitaline	$C_{54}H_{45}O_{30}$, a glucoside
Hyoscyamine	$C_{17}H_{23}NO_3$
Caffeine	$C_8H_{10}N_4O_2 \cdot H_2O$
Piperine	$C_{17}H_{19}NO_3$
Picrotoxine ; composition doubtful.	

Index.

The specimens of alkaloids and their derivatives, the strength of the solutions examined, the solvents employed, the sources whence the alkaloids were obtained, or by whom they were prepared, are given in the following tabular statement.

Double normal sulphuric acid signifies a gramme molecule of H_2SO_4 in a litre of liquid, or $\frac{H_2SO_4}{1000}$.

Name.	Proximate strength of solutions.	Solvent.	From whom obtained.	Page.
Aconitine, Plate 53, fig. 1	$\frac{1}{200}, \frac{1}{1000}$	Alcohol, sp. gr. 0·8	Dr. C. R. A. WRIGHT	479
Aconitine, Plate 53	$\frac{1}{200}$	Proof spirit	Dr. STEVENSON	479
Aconitine, Plate 53, fig. 2	$\frac{1}{200}, \frac{1}{1000}$	Alcohol, sp. gr. 0·8	T. and H. SMITH and Co.	480
Aconitine (foreign), Plate 53	$\frac{1}{200}$	" "	" "	481
Japaconitine, Plate 53, fig. 3	$\frac{1}{200}, \frac{1}{1000}$	" "	Dr. C. R. A. WRIGHT	481
Pseudaconitine (4), Pl. 53, fig. 4	$\frac{1}{200}, \frac{1}{1000}$	" "	" "	482
Aconitine	$\frac{1}{200}, \frac{1}{1000}, \frac{1}{5000}$	" "	Dr. STEVENSON	483
MORSON'S aconitine (5), Plate 53, fig. 5	$\frac{1}{200}, \frac{1}{1000}, \frac{1}{5000}$	" "	"	484
Aconitine (6), Plate 53, fig. 6	$\frac{1}{200}, \frac{1}{1000}, \frac{1}{5000}$	" "	"	485
Aconitine	$\frac{1}{200}, \frac{1}{1000}$	" "	"	486
Quinine, Plate 53, fig. 7	$\frac{1}{1000}$	" "	MR. DAVID HOWARD	487
Quinine sulphate, Plate 54	$\frac{1}{1250}$	Alcohol, sp. gr. 0·8, with $\frac{1}{4}$ volume of $\frac{H_2SO_4}{1000}$	" "	487
Cinchonine, Plate 54	$\frac{1}{1250}$		" "	488
Quinidine sulphate, Plate 54	$\frac{1}{1250}$		" "	488
Cinchonidine sulphate, Pl. 54	$\frac{1}{1250}$		" "	489

Name.	Proximate strength of solutions.	Solvent.	From whom obtained.	Page.
Morphine, Plate 54, fig. 5 . .	$\frac{1}{250}, \frac{1}{1000}$. . .	Alcohol, sp. gr. 0·8	T. and H. SMITH and Co.	489
Morphine, Plate 54, fig. 6 . .	$\frac{1}{250}, \frac{1}{1000}$. . .	" "	MACFARLAN and Co.	490
Tetracetyl-morphine, Plate 55	$\frac{1}{200}, \frac{1}{1000}$. . .	" "	Dr. C. R. A. WRIGHT	491
Codeïne, Plate 55, fig. 2 . .	$\frac{1}{200}, \frac{1}{1000}$. . .	" "	" "	492
Codeïne, Plate 55, fig. 3 . .	$\frac{1}{200}, \frac{1}{1000}$. . .	" "	T. and H. SMITH and Co.	492
Diacetyl-codeïne, Pl. 55, fig. 4	$\frac{1}{200}, \frac{1}{1000}$. . .	" "	Dr. C. R. A. WRIGHT	493
Thebaine, Plate 55, fig. 5 . .	$\frac{1}{200}, \frac{1}{250}, \frac{1}{1000},$ $\frac{1}{5000}$	" "	T. and H. SMITH and Co.	494
Papaverine	$\frac{1}{400}, \frac{1}{2000}, \frac{1}{5000}$.	" "	" "	495
Narcotine, Plate 55, fig. 6 . .	$\frac{1}{200}, \frac{1}{1000}, \frac{1}{5000}$.	" "	" "	497
Narceïne	$\frac{1}{250}, \frac{1}{1000}, \frac{1}{10000}$	" "	" "	498
Apomorphine hydrochloride, Plate 56, fig. 1	$\frac{1}{200}, \frac{1}{1000}, \frac{1}{5000},$ $\frac{1}{25000}$	" "	" "	501
Cotarnine hydrobromide . .	$\frac{1}{200}, \frac{1}{1000}, \frac{1}{10000}$	" "	Dr. C. R. A. WRIGHT	499
Veratrine, Plate 56, fig. 4 . .	$\frac{1}{200}, \frac{1}{1000}$. . .	" "	T. and H. SMITH and Co.	505
Cevadine	$\frac{1}{200}$	" "	Dr. C. R. A. WRIGHT	506
Brucine, Plate 56, fig. 5 . .	$\frac{1}{250}, \frac{1}{1000}, \frac{1}{5000}$.	" "	" "	506
Strychnine, Plate 56, fig. 6 .	$\frac{1}{250}, \frac{1}{500}, \frac{1}{2500},$ $\frac{1}{5000}, \frac{1}{12500}$	" "	" "	507
Piperine, Plate 56, fig. 3 . .	$\frac{1}{200}, \frac{1}{5000}$	" "	T. and H. SMITH and Co.	509
Oxynarcotine, Plate 56, fig. 2	$\frac{1}{250}, \frac{1}{1000}, \frac{1}{5000}$ $\frac{1}{25000}$	Absolute alcohol, with $\frac{1}{4}$ vol. glacial acetic acid	Dr. C. R. A. WRIGHT	502
Nicotine	$\frac{1}{100}$	Alcohol, sp. gr. 0·8	T. and H. SMITH and Co.	513
Solanine	$\frac{1}{250}$	" "	" "	511
Atropine	$\frac{1}{200}$	" "	" "	510
Hyoscyamine	$\frac{1}{200}$	" "	" "	511
Digitaline	$\frac{1}{250}$	" "	" "	512
Picrotoxine	$\frac{1}{200}$	" "	" "	512
Caffeïne	$\frac{1}{400}$	" "	" "	513

In all cases where the strength of the solutions have been stated as $\frac{1}{200}$ or $\frac{1}{1000}$, it is to be understood as one part by weight of the substance dissolved in liquid equal in volume to 200 times the weight of distilled water; thus 0·2 grm. dissolved in 40 cub. centims. of alcohol is represented by $\frac{1}{200}$ th; or 0·1 grm. dissolved in 20 cub. centims. of alcohol, to which 5 cub. centims. of acetic acid were added in order to prepare a perfectly clear solution, is indicated by $\frac{1}{250}$. In thus making the liquids up to proportionate volumes we avoid the complication of having to weigh the solvents, while in every case the cells of varying thicknesses represent proportional weights of the alkaloids.

The measurements and descriptions of spectra.

ACONITINE. From Dr. C. R. A. WRIGHT. Plate 53, fig. 1.

0.2 grm. in 40 cub. centims. of alcohol of 0.8 sp. gr.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2860
4	Continuous to	2860
3	Continuous to	2770
	ABSORPTION BAND	2799 to 2714
	Rays transmitted	2614
	Spectrum ends at.	2573
2	Continuous to	2747
	ABSORPTION BAND	2747 to 2614
	Rays transmitted very faintly till	2614
	Spectrum ends at.	2573
1	Continuous	2747
	Very weak	2746 to 2614
	Weak to.	2547

This solution, which had been prepared with dilute alcohol (proof spirit), was kept two years to ascertain whether it would undergo any change likely to make an alteration in its spectrum. About 20 cub. centims. were contained in a bottle holding 50 cub. centims., it was freely exposed to air in this manner, by occasional removals of the stopper, in order to subject it to the conditions which might affect an ordinary pharmaceutical preparation. It yielded the same spectrum before and after this period of keeping. In order to test whether violent chemical treatment might affect the spectrum, it was boiled with concentrated sulphuric acid for fifteen minutes, till all the alcohol was expelled; it was then diluted with a known volume of water and again examined, but it was found quite unaltered. It was not subjected to treatment with alkalis, though it is known that it may be thus converted into benzoic acid and a new base. If the treatment with sulphuric acid is sufficiently prolonged it equally effects this transformation, and there is less liability to darkening of the solution by the formation of resinous products than by saponification with alkaline solutions. The liquid should then show the absorption band characteristic of benzoic acid. (See Phil. Trans., Vol. 170, p. 257, 1879.)

ACONITINE. From Dr. STEVENSON.

0.2 gr. in 40 cub. centims. of alcohol of 0.8 sp. gr., or approximately 1 in 200.

Unfortunately, no exact measurements of this spectrum can be given, but the diagram which was made at the time when that of the previous sample of aconitine was drawn, was precisely the same, hence it may be inferred that the measurements were

the same. It is as well to mention here that the whole of this work was executed in 1882, some of it even at an earlier date, and curves were plotted according to the method described in the paper in the Phil. Trans., Vol. 170, p. 257, but two years subsequently the work was repeated, after the modifications in the method of working had been introduced.

ENGLISH ACONITINE. From Messrs. T. and H. SMITH and Co., of Edinburgh and London. Plate 53, fig. 2.

0·2 grm. in 40 cub. centims. of alcohol of 0·8 sp. gr.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong	3171
4	Continuous, strong	3171
	Faint	3138
3	Strong	3131
	Weak	3008
2	Continuous, strong	3128
	Weak	3008
	ABSORPTION BAND	3008 to 2747
	Rays transmitted, faint
	Spectrum ends at	2573
1	Continuous, strong	2978
	ABSORPTION BAND	2978 to 2872
	Rays transmitted, weak, to	2573
	Spectrum, faint, end at	2547

0·02 grm. in 20 cub. centims. of alcohol of 0·8 sp. gr.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3020
	Feeble to	2995
	ABSORPTION BAND	2995 to 2735
	Spectrum ends at	2556
4	Continuous, strong, to	2965
	ABSORPTION BAND	2965 to 2863
	Spectrum ends at	2556
3	Spectrum continuous to	2556
	Very feeble to	2518
2	Spectrum ends at	2466
1	Fairly strong, continuous spectrum to	2466
	Spectrum ends at	2255

FOREIGN ACONITINE. From Messrs. T. and H. SMITH and Co.

0.2 grm. in 40 cub. centims. of alcohol of 0.8 sp. gr.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2839
4	Continuous to	2839
3	Continuous to	2573
2	Continuous to	2547
1	The same spectrum, but stronger and extending to a faint ray	2486

JAPACONITINE. From Dr. C. R. A. WRIGHT. Plate 53, fig. 3.

0.2 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2861
4	Continuous to	2839
3	Continuous, strong	2861
	ABSORPTION BAND	2799 to 2614
	Spectrum ends at	2573
	From 2614 to 2573 the spectrum is only very faintly visible.	
2	Continuous	2747
	ABSORPTION BAND	2747 to 2614
	Spectrum ends at	2573
1	Rays transmitted to	2547
	Remains of the absorption band are seen in the very weak transmission of rays lying between	2747 and 2614
0.8	Rays transmitted to	2529
0.6	Rays transmitted to	2529
0.4	Rays transmitted to	2526
0.2	Continuous to	2429

This substance gave the same spectrum after a solution in weak alcohol (proof spirit) had been kept for two years.

PSEUDACONITINE. From Dr. C. R. A. WRIGHT. Plate 53, fig. 4.

0.2 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8.

This solution was diluted to five times its original volume for these photographs.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3127
4	Continuous, strong to	3084
3	Continuous, strong to	3028
	ABSORPTION BAND	3028 to 2431
	Rays faintly transmitted to where spectrum ends at	2316
2	Continuous to	2747
	ABSORPTION BAND	2747 to 2504
	Rays transmitted faintly to	2431
	Rays transmitted weakly to	2316
1	Continuous to	2316
	Spectrum ends at a line the position of which is just indicated . . .	2292

This substance yielded the same spectrum after it had been kept for two years in solution in weak alcohol (proof spirit).

A series of aconitines from different sources of manufacture was kindly sent to me by Dr. STEVENSON, Lecturer on Chemistry and Medical Jurisprudence at Guy's Hospital, London.

The list of specimens, which was accompanied by remarks upon them, is the following :—

No. 1. "Exotic aconitine, probably German, rather inert."

No. 2. "A fine specimen of crystallised aconitine, special, prepared by T. MORSON and SON, 124, Southampton Row, London."

No. 3. "Aconitine, from BURGOYNE, BURBIDGES and Co., 16, Coleman Street, London."

No. 4. "Nitrate of Aconitine." (This specimen was accidentally destroyed.)

No. 5. "Aconitine of uncertain source."

No. 1. ACONITINE. Exotic aconitine, probably German ; rather inert.

0.1 gm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
10	Continuous to	3245.5
9	Continuous to	3245.5
8	Continuous to	3245.5
7	Same as last	
6	Continuous to	3245.5
5	Continuous to	3130
	Spectrum extends feebly to	2863
4	Continuous to	2948
	Spectrum extends feebly, but not continuous to	2568
3	Continuous to	2948
	A feeble spectrum extends to	2568
2	Continuous strong to	2863
	A feeble spectrum extends to	2568
1	Continuous to	2863
	Spectrum extends weakly to	2568

0.1 in 20 dilutes 2 cub. centims. to 10 cub. centims., or 0.1 gm. in 100 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2863
	A feeble spectrum extends to	2568
4	Continuous spectrum to	2542
3	Same as last	
2	Continuous spectrum to	2472.5
1	Continuous to	2472.5
	Spectrum extends feebly to	2387

0.1 gm. in 500 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave lengths.
millims.		
5	Continuous to	2387
	Spectrum extends faintly to	2259
4	Same as last up to	2259
	Spectrum extends feebly to	2144
3	Same as last.	
2	Same as last, but stronger.	
1	Same as last.	

No. 2. ACONITINE. From F. MORSON and SON. Plate 53, fig. 5.

0·1 grm. in 20 cub. centims. of alcohol of sp. gr. 0·8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3130
4	Same as last.	
3	Continuous to	3130
2	Same as last.	
1	Continuous, strong to	3130

0·1 grm. in 100 cub. centims. of alcohol of sp. gr. 0·8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3085
4	Continuous to	3085
3	Continuous to	3033
	ABSORPTION BAND from	3033 to 2836·5
	Rays transmitted, not continuous to	2740
	ABSORPTION BAND from	2740 to 2424·3
	Rays transmitted very feebly to	2310
2	Continuous to	3002
	ABSORPTION BAND from	3002 to 2863
	Rays transmitted weakly to	2740
	ABSORPTION BAND from	2740 to 2424·3
	Rays transmitted weakly to	2310
1	Continuous to	2740
	Very feeble, but not continuous to	2440·5
	Very feebly continuous to	2286

0·1 grm. in 500 cub. centims. of alcohol of sp. gr. 0·8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2740
	Very feeble, but not continuous to	2440·5
	Feebly continuous to	2310
4	Continuous to	2696·5
	Very feebly continuous 205	205
	Faint but not continuous to	2472·5
	Feebly continuous to	2310
3	Some at last.	
2	Continuous to	2259
1	Continuous to	2259

No. 3. ACONITINE. From BURGoyNE, BURBIDGES and Co. Plate 53, fig. 6.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous	2976.5
4	Continuous to	2863
	ABSORPTION BAND from	2863 to 2613
	Rays transmitted at	2568
3	Continuous to	2863
	Weak, not continuous to	2740
	ABSORPTION BAND from	2740 to 2658
	Rays transmitted at	2568
2	Continuous to	2863
	Weak, but not continuous.	2568
1	Continuous to	2493.5

0.1 grm. in 100 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2493.5
4	Continuous to	2476
3	Continuous strong to	2476
2	Continuous to	2472.5
	Spectrum extends feebly to	2418
1	Continuous to	2418

There is a *weakening of the spectrum* between 2402 and 2310, but it can scarcely be called an *absorption band*.

0.1 grm. in 500 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2418
	<i>Weakening of the spectrum from</i>	2387 to 2310
	Rays transmitted feebly to	2259
4	Continuous to	2387
	Spectrum extends to	2145.9
3	Same as last.	
2	Same as last, but stronger.	
1	Continuous to	2190

No. 5. ACONITINE. Aconitine of uncertain source.

0·1 grm. in 20 cub. centims. of alcohol of sp. gr. 0·8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2812
	Spectrum faint, but not continuous, extends to	2568
4	Continuous to	2812
	Spectrum extends to	2568
3	Continuous to	2568
2	Continuous to	2542
1	Continuous to	2472·5

0·1 grm. in 100 cub. centims. of alcohol of sp. gr. 0·8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2472·5
4	Continuous to	2418
3	Same as last.	
2	Continuous to	2418
1	Continuous to	2387
	Spectrum extends to	2145·9

Of these specimens, the spectra of which have been described, only two exhibit absorption bands. Curves have been drawn of these.

MORSON'S preparation, the crystals of which were one and even two millimetres in length, was found to absorb the rays at two points, the two absorptions being equally strong. The measurements and descriptions of the transmitted spectra are here given, together with the curves.

It is noticeable that the most active aconitines are those with strongest absorption bands; and of the commercial samples scarcely two yield the same absorption spectra. The variations in the curves indicate that not only may there be considerable differences in their composition, but also in their chemical constitution.

QUININE. From Mr. DAVID HOWARD. Plate 53, fig. 7.

0.02 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3465
4	Continuous, strong to	3465
3	Continuous, strong to	3403
	ABSORPTION BAND from	3403 to 3033
	Rays transmitted to	2995.5
2	Continuous, strong to	3403
	ABSORPTION BAND from	3403 to 3033
	Rays transmitted very weakly to	2980
	ABSORPTION BAND, but weaker than former, from	2974 to 2854
	Rays transmitted very weakly to	2572
1	Continuous, strong to	3393
	*Feeble, but not continuous to	3123
	Continuous, strong to	2936
	*Feeble to	2880
	Continuous, weak to	2469

QUININE SULPHATE. From Mr. DAVID HOWARD. Plate 54, fig. 1.

0.02 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8, and 5 cub. centims. of double normal sulphuric acid.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3746
	ABSORPTION BAND from	3746 to 2865
	Rays transmitted to	2747
	Spectrum ends at	2660
4	Continuous to	3746
	ABSORPTION BAND from	3746 to 2875
	Spectrum ends at	2660
3	Continuous to	3691
	ABSORPTION BAND from	3691 to 3028
	Spectrum ends at	2644
2	Continuous, strong to	3606
	ABSORPTION BAND from	3606 to 3466
	Rays transmitted to	2632
1	Continuous, strong to	3606
	Weak, scarcely continuous to	3465
	This may be called a faint absorption band.	
	Continuous, strong to	2632
	Spectrum ends at	2515

* At these points there are traces of absorption bands. They may be said to be still there, but feeble.

CINCHONINE. From Mr. DAVID HOWARD. Plate 54, fig. 2.

0·02 grm. in 20 cub. centims. of alcohol of sp. gr. 0·8, and 5 cub. centims. of double normal sulphuric acid.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3465
	ABSORPTION BAND from	3465 to 2735·5
	Rays transmitted to	2569
4	Continuous to	3356
	ABSORPTION BAND from	3356 to 2834
	Rays transmitted to	2569
	Spectrum ends at	2544
3	Continuous to	3356
	ABSORPTION BAND from	3356 to 2834
	Spectrum ends at	2547
2	Continuous to	3260
	ABSORPTION BAND from	3260 to 2860
	Spectrum ends at	2467
1	Continuous, strong to	3260
	ABSORPTION BAND from	3260 to 3022
	Spectrum ends at	2467

QUINIDINE SULPHATE. From Mr. DAVID HOWARD. Plate 54, fig. 3.

0·02 grm. in 20 cub. centims. of alcohol of sp. gr. 0·8, with 5 cub. centims. of double normal sulphuric acid added.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3737
	ABSORPTION BAND from	3737 to 2867
	Spectrum ends at	2660
4	Continuous to	3690
	ABSORPTION BAND from	3690 to 2875
	Spectrum ends at
3	Continuous to	3691
	ABSORPTION BAND from	3691 to 2891
	Spectrum ends at	2644
2	Continuous to	3178
	ABSORPTION BAND from	3178 to 3022
	Spectrum ends at	2644
1	Continuous, strong to	3606
	Continuous, weak to	3461
	Continuous, strong to	2628
	Spectrum ends at	2610

CINCHONIDINE SULPHATE. From Mr. DAVID HOWARD. Plate 54, fig. 4.

0.02 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8, with 5 cub. centims. of double normal sulphuric acid added.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3364
	ABSORPTION BAND from	3364 to 2860
	Spectrum ends at	2614
4	Continuous to	3364
	ABSORPTION BAND from	3364 to 2860
	Spectrum ends at	2614
3	Continuous to	3348
	ABSORPTION BAND from	3348 to 2860
	Spectrum ends at	2614
2	Continuous to	3258
	ABSORPTION BAND from	3258 to 2864
	Spectrum ends at	2569
1	Continuous, strong to	3258
	<i>Absorption incomplete</i> from	3258 to 2907
	Spectrum ends at	2572

MORPHIA. From Messrs. T. and H. SMITH and Co, Plate 54, fig. 5.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3008
4	Strong, continuous to	3008
3	Continuous to	2980
2	Strong, continuous to	3008
	Rather weak to	2980
	ABSORPTION BAND	2980 to 2660
	Rays transmitted faintly to	2572
1	Continuous to	2957
	ABSORPTION BAND	2956 to 2747
	Rays transmitted to	2572

0.1 grm. in 10 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	2980
	ABSORPTION BAND	2980 to 2747
	Rays transmitted weakly to end at	2572
4	Continuous, strong to	2949
	ABSORPTION BAND	2949 to 2838
	Spectrum ends at	2572
3	Continuous to	2980
	ABSORPTION BAND	2949 to 2870
	Spectrum ends at	2547
1	Continuous, but rather weak.	2504
	Rays transmitted feebly	2316
	Spectrum ends at	2316

MORPHINE. From MACFARLAN and Co., Edinburgh. Plate 54, fig. 6.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous.	3008
4	Same as five.	
3	Continuous to	3008
	ABSORPTION BAND	3008 to 2613
2	Continuous to	2980
	ABSORPTION BAND	2980 to 2613
	Rays feebly transmitted to	2570
1	Continuous to	3008
	ABSORPTION BAND from	2980 to 2836
	Rays feebly transmitted to	2570

Solution of 0.1 in 25 cub. centims. of alcohol of sp. gr. 0.8, diluted to four times its volume, equivalent to 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
4	Continuous to	2980
	ABSORPTION BAND from	2980 to 2836
	Rays feebly transmitted to	2570
3	Continuous to	2980
	ABSORPTION BAND	2980 to 2857
	Rays transmitted feebly at	2570
2	Continuous to	2980
	ABSORPTION BAND	2980 to 2880
	Rays transmitted to	2542
1	Continuous to	2980
	Very feebly continuous to	2542

TETRACETYL-MORPHINE. From Dr. C. R. A. WRIGHT. Plate 55, fig. 1.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2949
4	Continuous to	2949
3	Continuous to	2926
	ABSORPTION BAND from	2926 to 2572
	Rays transmitted very faintly	2572
2	Continuous to	2902
	ABSORPTION BAND from	2902 to 2611
	Rays transmitted faintly to	2547
1	Continuous to	2864
	ABSORPTION BAND from	2864 to 2745
	Rays transmitted to	2544

Should there appear to be any discrepancy between the measurements of absorption bands seen in the spectra of strong and weak solutions of the same substance which might be expected to give the same readings on the scale, they may be accounted for by the fact that two series of photographs were taken by different persons and the measurements made and recorded by different observers, the later observations being made after the lapse of several months. In no case have the differences between any two sets of measurements been sufficiently great to affect the curves.

0.2 grm. in 200 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	2965
	ABSORPTION BAND	2964 to 2601
	Spectrum ends at	2556.5
4	Continuous to	2821.5
	ABSORPTION BAND	2821 to 2735
	Spectrum ends at	2535.5
3	Rays continuous to	2821.5
	Rays transmitted feebly to	2593
	A little stronger to	2556.5
	Very feebly transmitted to where spectrum ends at	2482
2	Spectrum ends at	2387
1	Spectrum ends at	2302.3

CODEINE. From Dr. C. R. A. WRIGHT. Plate 55, fig. 2.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3008
4	Continuous to	2980
3	Continuous to	2980
2	Continuous, strong to	2980
	ABSORPTION BAND from	2977 to 2613
	Rays transmitted at	2613
1	Continuous, strong to	2977
	ABSORPTION BAND from	2977 to 2747
	Rays transmitted to	2572

0.02 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	2965
4	Continuous to	2965
	ABSORPTION BAND	2965 to 2735
	Spectrum ends at	2556
3	Continuous to	2942
	ABSORPTION BAND	2942 to 2798
	Spectrum ends at	2556
2	Continuous to	2942
	ABSORPTION BAND	2942 to 2863
	Rays transmitted to	2556
1	Spectrum strong to	2942
	Rays transmitted are weak to end at .	2556

CODEINE. From Messrs. T. and H. SMITH and Co. Plate 55, fig. 3.

0.2 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Strong, continuous to	3008
4	Strong, continuous to	3008
	Very faint to	2980
3	Strong, continuous to	3008
	Faint to	2980
2	Strong, continuous to	2980
	ABSORPTION BAND	2964 to 2660
	Rays transmitted faintly to	2613
1	Continuous, strong to	2980
	ABSORPTION BAND	2747 to 2572
		transmitted
	Continuous, strong to	2980
	ABSORPTION BAND	2962 to 2747
	Rays transmitted to	2572

The original solution diluted to 5 times its original volume=1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2976
	ABSORPTION BAND	2962 to 2747
	Rays transmitted to	2613
4	Continuous to	2976
	ABSORPTION BAND	2976 to 2747
	Rays transmitted to	2570
3	Continuous to	2976
	ABSORPTION BAND	2976 to 2747
	Rays transmitted to	2570
2	Continuous to	2976
	ABSORPTION BAND	2976 to 2740
	Rays faintly transmitted to	2740
	Very faint at	2568
1	Continuous to	2875
	Spectrum ends at	2542

DIACETYL-CODEINE. From Dr. C. R. A. WRIGHT. Plate 55, fig. 4.

0.2 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5-4-3	Continuous, strong in all three cases to	2976
2	Continuous to	2947
	ABSORPTION BAND	2947 to 2613
	Rays transmitted to	2572

The original solution was diluted to 5 times its original volume=1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	2976
	ABSORPTION BAND	2976 to 2609
	Rays transmitted to	2568
4	Continuous, strong to	2942
	ABSORPTION BAND	2942 to 2740
	Rays transmitted to	2568
3	Continuous, strong to	2942
	ABSORPTION BAND	2942 to 2740
	Rays transmitted to	2556
2	Continuous to	2556
	Rays transmitted at	2542
1	The same to	2542
	Rays transmitted feebly to	2210

THEBAÏNE. From T. and H. SMITH and Co. Plate 55, fig. 5.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8 or 1 in 250.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3250
4	Continuous, strong to	3250
	Faint to	3230
	Very faint to	3174
3	Continuous, strong to	3250
	Faint to	3174
2	Continuous, strong to	3250
	Weak to	3174
1	Continuous, strong to	3250
	Rather weak to	3174
	Faint to	2265*

A diluted solution of this showed an abnormal absorption at one end of the spectrum, *i.e.*, 5 millims. dilute should be equivalent to 1 millim. undilute, dilution being five times; probably due to a change in the solution from being kept.

0.1 in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3238
	Feebly continuous to	3215.5
4	Continuous, strong to	3238
	Feebly continuous to	3215.5
3	Continuous to	3171
2	Continuous to	3171
1	Continuous to	3171

0.1 grm. 20 cub. centims. of alcohol of sp. gr. 0.8, diluted 2 cub. centims. to 10 cub. centims. = 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave lengths.
millims.		
5	Continuous, strong to	3238
	Weak, continuous to	3171
4	Continuous to	3140
3	Continuous to	3123.5
2	Continuous to	3123.5
	ABSORPTION BAND from	3171 to 2568
1	Continuous to	3171
	ABSORPTION BAND from	3171 to 2568
	Rays transmitted to	2568

* It is remarkable how the spectrum suddenly lengthens at this point.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8, diluted 2 cub. centims. to 50 cub. centims. = 1 in 5000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3123.5
	ABSORPTION BAND from	3171 to 2568
	Rays transmitted faintly to	2490.5
4	Continuous to	2976.5
	ABSORPTION BAND from	2976.5 to 2740
	Rays transmitted to	2469.5
3	Continuous to	2976.5
	ABSORPTION BAND	2976.5 to 2863
	Rays transmitted to	2418
2	Continuous to	2863
	<i>Fairly strong but not continuous</i>	2863 to 2653
	Continuous to	2472.5
1	Continuous to	2466

PAPAVERINE. From T. and H. SMITH and Co.

0.1 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3403
4	Continuous, strong to	3403
3	Continuous, strong to	3403
	Continuous, weak to	3352
2	Continuous, strong to	3352
1	Continuous, strong to	3352
	Faint to	3330

0.1 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8, diluted 2 cub. centims. to 10 cub. centims.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3982
	Faint to	3468
4	Continuous, faint to	3352
3	Continuous to	3352
2	Continuous to	3330
1	Continuous to	2980

0.1 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8.

This solution was kept for some time previous to being photographed.

Thickness of layer of liquid.	Description of Spectrum.	Wave-lengths.
millims.		
5	Very faint to	4237
4	Faint to	4237
3	Weak, continuous to	4237
	Spectrum extends to	3982
2	Continuous to	3982
	Faint to	3600
1	Continuous to	3456

0.1 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8, diluted 2 cub. centims. to 10 cub. centims. or 1 in 2000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3456
4	Continuous to	3340
3	Continuous to	3324
2	Continuous to	3002
1	Continuous to	2740

0.1 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8, diluted to 1 in 2000, again diluted 2 cub. centims. to 10 cub. centims. or 1 in 10,000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2740
4	Weak, continuous to	2568
3	Same as last spectrum.	
2	Rays transmitted to	2568
1	Continuous to	2545
	ABSORPTION BAND, from	2545 to 2343
	Rays transmitted faintly to	2265

0.1 grm. in 40 cub. centims. of alcohol of sp. gr. 0.8, third dilution or 1 in 50,000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to termination of spectrum	2572
4	Continuous to	2545
	Ill-defined ABSORPTION BAND from	2545 to 2313
	Rays transmitted feebly to	2265
3	Very strong, continuous to	2862
	Continuous, and fairly strong to	2572
	Ill-defined ABSORPTION BAND from	2545 to 2313
	Rays transmitted to	2265
2	The same description and measurement are applicable, the lines being a little stronger.	
1	Continuous to	2572
	ABSORPTION BAND visible	2545 to 2313
	But lines are transmitted very feebly { at {	2495, 2483, 2429, 2422, 2355
	Spectrum ends at.	2255

NARCOTINE. From Messrs. T. and H. SMITH and Co. Plate 55, fig. 6.

0.2 grm. dissolved in 20 cub. centims. of alcohol of sp. gr. 0.8 = 1 in 200.

Thickness of layer of liquid.	Description of spectrum.	Wave lengths.
millims.		
5	Strong, continuous to	3464
4	Strong, continuous to	3403
3	Strong, continuous to	3403
2	Strong, continuous to	3352
1	Strong, continuous to	3352

0.2 dissolved in 200 cub. centims. of alcohol of sp. gr. 0.8 = 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Strong, continuous to	3352
	Somewhat doubtful trace.	
4	Strong, continuous to	3352
	ABSORPTION BAND from	3330 to 2707
	Rays transmitted to	2705
3	Strong, continuous to	3330
	ABSORPTION BAND from	3262 to 2839
	Rays weakly transmitted to	2572
2	Strong, continuous to	3330
	ABSORPTION BAND from	3262 to 2839
	Rays transmitted to	2572
1	Strong, continuous to	3260
	Spectrum continuously transmitted to	2545

0.2 dissolved in 200 cub. centims. of alcohol of sp. gr. 0.8, 2 cub. centims. diluted to
10 = 1 in 5000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Strong, continuous to	3245.5
	Weakening of the spectrum between .	3245.5 and 2863
	Continuous to	2482.5
4	Continuous to	2418
3	Continuous to	2418
2	Continuous to	2310
1	Continuous to	2259

NARCEINE. From T. and H. SMITH and Co.

0.1 grm. in 25 cub. centims. or 20 cub. centims. of alcohol of sp. gr. 0.8, with
5 cub. centims. of glacial acetic acid added thereto.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3572
	Weak to	3465
4	Continuous, strong to	3465
	Weak to	3330
3	Continuous to	3330
	Faint to	3276
2	Continuous to	3260
1	Continuous, strong to 119	3260

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8. Solution kept some time.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Faint, continuous to	4237
	Feebly continuous to	4041
4	Weak, continuous to	4041
	Faint, continuous to	3982
3	Same as last.	
2	Fairly strong, continuous to	3982
	Feebly continuous to	3600
1	Fairly strong, continuous to	3982
	Faint to	3456

2 cub. centims. of 0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8, diluted to 8 cub. centims.=1 in 1000

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
4	Continuous to	3245.5
3	Same as last spectrum.	
2	Continuous to	3171
1	Continuous to	3008

2 cub. centims. of 0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8, diluted to 80 cub. centims.=1 in 10,000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
10	Continuous to	2740
9	Same as last spectrum.	
8	Same as last spectrum.	
7	Same as last spectrum, but slightly stronger.	
6	Same as last spectrum.	
5	Same as last spectrum.	
4	Same as last, stronger.	
3	Continuous to	2418
2	Continuous to	2418
1	Continuous to	2310

COTARNINE HYDROBROMIDE. From Dr. C. R. A. WRIGHT.

The original solution $\frac{1}{200}$ diluted to five times its volume, or 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	4143
	ABSORPTION BAND	4061 to 2747
4	Continuous to	4061
	ABSORPTION BAND	4061 to 2747
3	The spectrum is substantially the same as that transmitted by 4 millims.	
2	Continuous to	3982
	ABSORPTION BAND	3982 to 2747
	Spectrum extends to	2696
1	Continuous as above to	3982
	ABSORPTION BAND	3982 to 2872
	Rays transmitted weakly to	2696

1 in 10,000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
10	Continuous to	3917
	ABSORPTION BAND	3982 to 2747
	The absorption is weakening and rays appear feebly, though in reality strong lines, as far as.	3800 3739 3682
	Rays very feebly transmitted to	2863
	Continuous, but weak to	2747
9	Continuous to	3600
	ABSORPTION BAND	3600 to 3033
	Rays feebly continuous to	2653
8	Continuous to	3600
	ABSORPTION BAND	3600 to 3033
	Rays continuous but feeble to	2653
7	The description of the spectrum trans- mitted by 8 millims. is the same, with the exception of a trace of a line at	2310
6	Spectrum precisely the same as 7 millims.	
5	Spectrum precisely the same as the foregoing as far as	2653
	Apparently an ABSORPTION BAND	2740 to 2310
	Rays feebly transmitted to	2310
4	Precisely the same as above, but in addition to the rays transmitted weakly to.	2310
	There are others extending to	2255
3	Continuous.	3600
	ABSORPTION BAND.	3600 to 3033
	This band is greatly weakened, so that rays are faintly transmitted to.	3033
	Continuous to	2740
	ABSORPTION BAND.	2740 to 2310
	Rays transmitted, the absorption being weakened between 2740 and	2568
	Also from 2430 to	2255
2	Continuous to	2863
	Continuous to	2740
	ABSORPTION BAND, diminished in inten- sity.	2740 to 2310
	Rays transmitted weakly to	2568
	Very feebly to	2255

APOMORPHINE HYDROCHLORIDE. From T. and H. SMITH and Co. Plate 56, fig. 1.

0.1 gram. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3465
4	Continuous, strong to	3465
3	Continuous, strong to	3465
	Faint to	3434
2	Continuous, strong to	3465
	Faint to	3403
1	Continuous to	3330

0.1 gram. in 20 cub. centims. of alcohol of sp. gr. 0.8 or 1 in 200. Fresh solution.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Weak, continuous to	3456
4	Weak, continuous to	3456
3	Weak, continuous to	3438
2	Weak, continuous to	3403
1	Fairly strong, continuous to	3982
	Weak, continuous to	3403

0.1 gram. in 20 cub. centims. 2 cub. centims. diluted to 10 cub. centims. = 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3403
4	Continuous to	3403
3	Continuous to	3403
	Faint to	3331.5
2	Continuous to	3261
1	Continuous to	3261
	Feeble lines at	3072

2 cub. centims. of the last solution diluted to 10 cub. centims. = 1 in 5000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3261
4	Same as last, but a little stronger	
3	Continuous to	3245.5
2	Continuous to	3245.5
	ABSORPTION BAND from	2976.5 to 2568
	Trace of a line at	2479.5

Three solutions of oxynarcotine were examined, this solution, which was kept for some time after the notes written below had been taken, yielded a spectrum from which the curve was drawn. It was found however that the liquid had undergone great change, so a second solution was made which yielded the dotted curve when quite fresh.

OXYNARCOTINE. From Dr. C. R. A. WRIGHT. Plate 56, fig. 2.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8 and 5 cub. centims. of acetic acid.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3465
4	Continuous to	3348
3	Continuous to	3332
2	Continuous to	3268
1	Continuous to	3186

Another solution of the same specimen, examined immediately after its preparation.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8 and 5 cub. centims. of acetic acid.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3456
	Two weak lines at }	
4	Continuous to	3324
3	Continuous	3245.5
2	Continuous to	3245.5
1	Continuous to	3245.5

2 cub. centims. diluted to 10 cub. centims. = 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
4	Continuous, strong to	3245.5
3	Continuous, strong to	3245.5
2	Continuous to	3171
1	Continuous to	3123.5

2 cub. centims. of the last solution diluted to 10 cub. centims. = 1 in 5000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims. 5	Continuous to AN ABSORPTION BAND from	3033 3008 to 2568
	Rays feebly transmitted at the following points	2976·5 2857·5 2836·5 2545
4	Continuous to ABSORPTION BAND from	3033 3008 to 2568
	Rays transmitted at the following points (spectrum not continuous)	2976·5 2857·5 2836·5 2744·5 2705 2597 2545 2497 2482·5 2430·7 2421
3	Continuous to Two strong lines at	3033
2	Spectrum extends to Same as last spectrum. The lines being a little stronger.	2421
1	Continuous to Spectrum extends to (not continuous)	2863 2310

2 cub. centims. of the last solution diluted to 10 cub. centims. = 1 in 25,000.

Thickness of layer of liquid.	Description of spectrum.	Wave lengths.
millims. 5	Continuous Spectrum extends to (not continuous)	2482·5 2310
4	Continuous Spectrum extends to (not continuous)	2418 2259
3	Same as last spectrum.	
2	Continuous Spectrum ends at	2310 2259
1	Same as last.	

The selective absorption in this substance is very slight, beginning at a thickness of 5 millims. and ending at the next thickness of 4 millims. in a solution of 1 gm. in 5000 cub. centims. (alcohol).

This solution gives a blue fluorescence similar to that given by pseudaconitine and apomorphine-hydrochloride.

A solution which had been kept for about six months and had evidently become altered.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8, and 5 cub. centims. of acetic acid or 1 in 250.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Faint to	4376
4	Feebly continuous to	4340
3	Feebly continuous to	4340
2	Feebly continuous to	4340
1	Weak, continuous to	4255

This substance gave a blue fluorescence similar to pseudaconitine and apomorphine-hydrochloride.

2 cub. centims. of the last solution diluted to 8 cub. centims. = 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
4	Weak, continuous to	3994
3	Continuous to	3994
2	Continuous to	3825
	To wave-length 3600 the spectrum is discontinuous.	
1.8	Continuous to	3825
	To wave-length 3600 the spectrum is feeble and discontinuous	
1.6	Continuous to	3825
1.4	Continuous to	3825
	ABSORPTION BAND from	3456 to 2740
	Rays transmitted to	2740
1.2	Continuous to	3825
	Rays are transmitted as far as wave-length 3456, but the spectrum is not continuous.	
	ABSORPTION BAND from	3456 to 2740
	Rays transmitted to	2740
1	Continuous to	3600
	Weak, but not continuous, to	2709.5

2 cub. centims. diluted to 20 cub. centims. = 1 in 10,000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
10	Continuous to	3610
	Very feebly continuous from	3600 to 3456
	Weakening of the spectrum between .	3171 and 2863
9	Same as last, but stronger.	
8	Same as last, with this exception.	
7	Same as last.	
6	Strong, continuous	3982
	Weak, continuous to	3600
	Rays transmitted to	2568
5	Strong, continuous to	3245.5
	Weak, continuous.	
	Faint, continuous to	2568
	Not continuous, but the lines are strongly marked to	2545
4	Continuous to	3245.5
	Spectrum extends to	2421
3	This spectrum is continuous to . . .	2310
2	Continuous spectrum to	2259
1	Same as last spectrum, but slightly stronger all through.	

VERATRINE. From Messrs. T. and H. SMITH and Co. Plate 56, fig. 4.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3145
4	Continuous to	3132
3	Continuous to	3111
2	Continuous to	3034
	ABSORPTION BAND	3034 to 2848
	Rays weakly transmitted to	2747
1	Continuous to	3016
	ABSORPTION BAND	3016 to 2860
	Rays transmitted to	2747
	Rays weakly transmitted to end of spectrum at	2707

0.1 grm. in 100 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3008
	ABSORPTION BAND	3008 to 2847
	Rays transmitted faint to	2740
4	Continuous to	3033
	ABSORPTION BAND	2976.5 to 2869
	Rays transmitted to	2705
3	Continuous to	3033
	Rays transmitted feebly and continuously to	2869
2	Continuous to	3171
	Weak to	2418
1	Continuous to	2307.5

CEVADINE. From Dr. C. R. A. WRIGHT (MERCK'S Veratrine).

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
	A thickness of liquid equal to 20 millims. transmits all rays strongly to	2735
5	Transmits all to	2556
1	Transmits all to	2518
	<i>No absorption band visible.</i>	

BRUCINE. Plate 56, fig. 5.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3246
4	Continuous, strong to	3246
3	Continuous, strong to	3246
2	Continuous, strong to	3246
1	Continuous, strong to	3246

0.1 grm. in 25 cub. centims. 2 cub. centims. diluted to 8 cub. centims. =1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3208
4	Continuous to	3171
3	Continuous to	3171
2	Continuous to	3171
1	Continuous to	3171
	ABSORPTION BAND from	3171 to 2857
	Rays transmitted to	2831.5
	ABSORPTION BAND from	2831.5 to 2427.5
	Rays transmitted to	2418

2 cub. centims. of the last solution diluted to 10 cub. centims. =1 in 5000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	3171
	ABSORPTION BAND from	3171 to 2857
	Rays transmitted to	2793
	ABSORPTION BAND from	2793 to 2424.3
	Rays transmitted to	2418
4	Continuous, strong to	3171
	FEEBLE ABSORPTION BAND	3171 to 2869
	Rays are transmitted feebly all through this band, and extend stronger from 2869 to	2740
	<i>Absorption band from</i>	2740 to 2568
	Rays transmitted to	2310
3	Continuous to	2310
2	Continuous to	2836.5
	Weak to	2310
	Faint to	2259
1	Continuous to	2259

STRYCHNINE. Plate 56, fig. 6.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	2976
4	Continuous, strong to	2976
3	Continuous, strong to	2976
2	Continuous, strong to	2976
	Very faint to	2946
1	Continuous, strong to	2976
	Weak to	2946

0.1 grm. in 50 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Strong, continuous to	2976.5
4	Strong, continuous to	2976.5
3	Strong, continuous to	2976.5
2	Strong, continuous to	2976.5
1	Strong, continuous to	2976.5
	Faint, continuous to	2948

2 cub. centims. of the last solution diluted to 10 cub. centims. = 1 in 2500.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2948
	Weak lines at	2863
	And	2836.5
	Trace of a line at	2740
4	Continuous to	2948
	Faint to	2740
3	Continuous to	2948
	Weak to	2740
	Faint line at	2701
	ABSORPTION BAND	2740 to 2310
	Rays transmitted at	2310
2	Continuous to	2740
	ABSORPTION BAND	2740 to 2310
	Rays transmitted from	2740 to 2701
	Also from (very faint)	2352 to 2259
1	Continuous to	2740
	ABSORPTION BAND	2568 to 2427.5
	Rays transmitted to	2259

2 cub. centims. of the last solution diluted to 10 cub. centims. = 1 in 12,500.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous to	2740
	ABSORPTION BAND	2568 to 2427.5
	Rays transmitted to	2259
	Two very faint lines at	2493.5
		2482.5
4	Continuous to	2259
3	Continuous to	2259
2	Continuous to	2259
1	Continuous to	2193

PIPERINE. From T. and H. SMITH and Co. Plate 56, fig. 3.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8. (1 in 200 cub. centims.)

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, fairly strong to	4061
4	Continuous, fairly strong to	4061
	Continuous, fairly weak to	4028
3	Continuous, strong to	4028
	Continuous, faint to	4000
2	Continuous, strong to	4000
1	Continuous, strong to	4000
	Continuous, weak to	3952

This solution was kept twelve months before the next series of photographs was taken.

The following measurements are the more exact, though there is but little difference between them.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3982
4	Continuous, strong to	3982
3	Continuous, strong to	3982
	Faint, continuous to	3955
2	Continuous, strong to	3982
	Faint, continuous to	3955
1	Same as last.	

2 cub. centims. of the last solution diluted to 10 cub. centims. = 1 in 1000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3982
	Faint, continuous to	3917
4	Continuous, strong to	3891
	Faint, continuous to	3825
3	Continuous, strong to	3891
	Faint, continuous to	3825
	Faint line at	3788
2	Continuous, strong to	3891
	Weak, continuous to	3825
	Weak line at	3788
1	Continuous, strong to	3825
	Weak to	3742
	Faint line at	3673

2 cub. centims. of the last solution diluted to 10 cub. centims. = 1 in 5000.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3825
	Weak to	3742
	Weak line at	3673
4	Continuous, strong to	3825
	Weak, continuous to	3706
	Faint to	3600
3	Continuous to	3600
	ABSORPTION BAND from	3600 to 2740
2	Continuous to	3600
	ABSORPTION BAND from	3600 to 2740
	Rays transmitted from	3600 to 3456
	Also from	2813 to 2568
	ABSORPTION BAND from	2568 to 2310
	With two lines faintly transmitted at {	2427·5
		2418
1	Continuous spectrum with indications of the absorption bands to	2201

ATROPINE. From T. and H. SMITH and Co.

0·1 grm. in 20 cub. centims. of alcohol of sp. gr. 0·8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
20	Continuous, strong to	2707
5	Continuous, strong to	2707
	Very faint as far as	2429
4	Continuous, strong to	2644
	Weak to	2573
	Very weak to	2429
3	Continuous, strong to	2573
	Rather weak to	2429
	Very faint extension to.	2398
2	Continuous, strong to	2398
	Very faint to about	2355
1	Continuous, strong to	2398
	Weak to	2355
	Very faint to	2340

SOLANINE. From T. and H. SMITH and Co.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Strong, continuous to	2570
	Weak to.	2265
4	Nothing characteristic	
3	Nothing characteristic	
2	Nothing characteristic	
1	Strong, continuous to	2265

A thickness of liquid as great as 20 millims. transmits all rays without selective absorption as far as 249, a faint appearance of a line at 256 and at 276 and at 293 are just sufficiently visible to be recorded.

HYOSCYAMINE. From T. and H. SMITH and Co.

0.1 grm. in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	2747
	Continuous, faint to.	2572
4	Continuous, strong to	2747
	Continuous, faint to.	2572
	Continuous, very faint to	2436
3	Continuous, fairly strong to	2613
	Continuous, weak to.	2572
	Continuous, faint to.	2430
2	Continuous, strong to	2572
	Continuous, weak to.	2430
	Continuous, faint to.	2422

A thickness of 20 millims. absorbs no less refrangible ray than $206.6=2747$. No band distinctly visible.

DIGITALINE. From T. and H. SMITH and Co.

0.1 grm. in 25 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	3610
	Very faint to	3465
	Exceedingly faint to.	3033
4	Continuous, strong to	3610
	Weak to.	3465
	Faint to	2572
3	Continuous, strong to	3465
	Weak to.	2980
	Faint to	2572
2	Continuous, fairly strong to	2837
	Fairly strong to	2572
	Faint to	2422
1	Continuous, strong, but not of normal strength to	2545
	Weak to.	2313

Thicker layers of liquid, namely, 10 millims., 15 millims., and 20 millims., were examined, but the absorption was continuous and increased down to transmission of rays at 75.

PICROTOXINE. From T. and H. SMITH and Co.

0.1 in 20 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Continuous, strong to	2398
	Very weak to	2261
4	The same increasing in strength.	
3	The same.	
2	Continuous and fairly strong	2261
1	Continuous and strong	2261
20	Continuous, strong to	2521
10	Continuous, strong to	2500
	Weak to.	2418

This substance shows no absorption band.

NICOTINE. From T. and H. SMITH and Co.

0.367 in 36.7 cub. centims. of alcohol of sp. gr. 0.8.

This substance exhibits no absorption band.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
20	Continuous, strong to	
5	Continuous, strong to	3132
	Weak to	3008
4	Continuous, strong to	3033
	Continuous, weak to	2980
3	Continuous, strong to	3033
	Continuous, weak to	2977
2	Continuous, strong to	2977
	Continuous, weak to	2947
	Continuous, very faint to	2834
1	Continuous, strong to	2875
	Continuous, weak to	2801

CAFFEINE. From T. and H. Smith and Co.

0.1 in 40 cub. centims. of alcohol of sp. gr. 0.8.

Thickness of layer of liquid.	Description of spectrum.	Wave-lengths.
millims.		
5	Transmits all rays to	2965
1	All to.	2942
	No absorption band visible.	

Having recently examined the spectra transmitted by pyridine, piperidine, quinoline, tetrahydroquinoline, and the hydrochlorides of these bases, it has been found that the absorption band of pyridine does not appear in the spectrum transmitted by piperidine, and that quinoline and tetra-hydroquinoline exhibit selective absorption very strongly, the curves differing from each other and from those of their hydrochlorides. Observations made on simple bases differ from those made on substitution products in this way that the bases are the more diactinic, while addition products are more diactinic than the bases.

SUMMARY.

Many alkaloids are capable of saponification, the products of the reaction are a new base and an organic acid which is frequently of the aromatic series.

The acid is not invariably of the aromatic series, otherwise its presence would

probably be evident in the absorption spectrum of the alkaloids. There are, however, two conditions under which an aromatic derivative would certainly not affect the spectrum in a characteristic manner, and these are, when the acid is a hydrogenised body like hydrophthalic acid, or when the basic portion of the molecule has so powerfully absorbed the rays that the band of selective absorption is obscured. The spectrum of narceïne is undoubtedly of this character, and so likewise is that of oxynarcotine. In order to comment upon the nature of the various absorption spectra described, it will be advantageous to refer briefly to what is at present known concerning the constitution of some of the alkaloids.

Alkaloids may be divided into two groups: (*a*) those which exhibit spectra with absorption bands; and (*b*) those which transmit continuous spectra.

ALKALOIDS and derivatives exhibiting spectra with absorption bands.

Aconitine	Papaverine	Cinchonine-sulphate
Pseudaconitine	Oxynarcotine	Quinidine-sulphate
Japaconitine	Apomorphine-hydrochloride	Cinchonidine-sulphate
Morphine	Tetra-acetyl-morphine	Veratrine
Narcotine	Di-acetyl-codeïne	Piperine
Codeïne	Quinine	Brucine
Thebaine	Quinine-sulphate	Strychnine

ALKALOIDS yielding continuous spectra.

Narceïne	Solamine	Picrotoxine
Aconitine (foreign)	Hyoscyamine	Nicotine
Cevadine	Digitaline	Caffeïne
Atropine		

The properties of the aconitines.

By saponifying the aconitines with acids, alkalies, or even with water at a high temperature under pressure, aconitine, japaconitine, and picraconitine yield benzoic acid and a new base, while pseudaconitine furnishes di-methyl-protocatechuic acid $C_6H_3 \left\{ \begin{matrix} (OCH_3)_2 \\ COOH \end{matrix} \right.$. It was thought probable that by the action of bromine on the alkaloids substitution would occur in the benzene nucleus, and a definite absorption of a pronounced character would result. This was however not the case, probably because the alkaloids were altogether altered, for after treatment they exhibited no absorption bands. In comparing the diagrams it is interesting to note the difference between pseudaconitine and the other aconitine bases, it evidently possesses a nucleus with a similar constitution, but the acid residue which is different modifies the absorption curve.

It has been shown by the researches of Dr. C. R. A. WRIGHT that the aconitines all yield apo-derivatives with such facility that to obtain the bases free therefrom is not an easy matter, and further they undergo saponification by acids and alkalies, very readily yielding an inert base in each case. Hence different preparations yield different absorption curves. The aconitine and japaconitine of Dr. WRIGHT have practically the same absorption spectrum and yield similar curves, but that of japaconitine is just what we might expect from a body with a nucleus of a similar constitution but twice the molecular weight of aconitine, namely, a much greater absorptive power. It has been shown that japaconitine has such a difference, for it is in fact a sesqui-apo-aconitine.*

The English aconitine of Messrs. T. and H. SMITH and Co. appears to be a modified form of japaconitine, and it is possible that the modification of the spectrum curve is in part due to an admixture of another body.

Foreign aconitine is doubtless an entirely different substance, since it yields no absorption bands, and it is known to be comparatively inactive physiologically.

On two separate occasions it was found necessary to estimate the strength of solutions of aconitine, and this was in each case successfully accomplished by taking a series of photographs and constructing a curve therefrom. That the results so obtained were correct was proved by a discovery of some missing notes giving particulars of the preparation of the solutions.

The constitution of the cinchona bases.

The examination of these bases was made by me five years ago, and although there were no means of obtaining accurate measurements of wave-lengths of the absorbed rays at that time, owing to the requisite data being wanting, yet some idea of the constitution of quinine and cinchonine was derived from a comparison of the absorption bands seen in the spectra of the substances themselves and of their derivatives and decomposition products.

The bands in the case of quinine and cinchonine extend into a region of less refrangibility than the absorption caused by pyridine, at the same time the position of the band agrees with that of quinoline.

In one of a series of papers contributed to the 'Transactions of the Chemical Society,' vol. xli., p. 45 ("Researches on the Relation of the Molecular Structure of Carbon Compounds to their Absorption Spectra."—Part VI.), I remarked that the quinine spectrum was probably due to the conjugation of four pyridine or two quinoline nuclei. Since then, several researches on the cinchona alkaloids have extended our knowledge, and formulæ have been proposed for quinine and for

* Vide the structural formulæ in the papers by WRIGHT and LUFF, and WRIGHT and MENKE, J. Chem. Soc., vol. xxxiii., p. 173; vol. xxxv., p. 404.

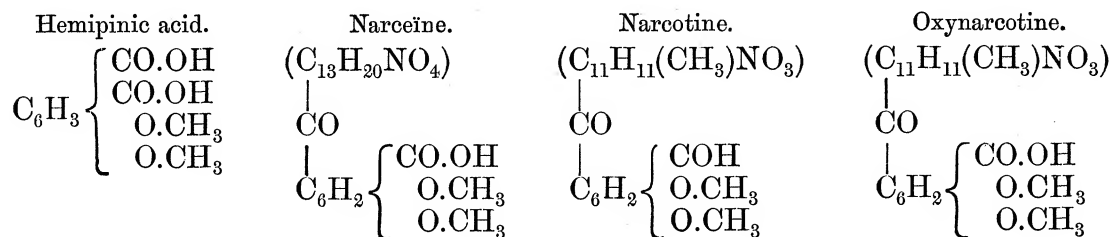
cinchonine by WISCHNEGRADSKY, WEIDEL, KÖENIGS, and SKRAUP, in all of which a more or less modified quinoline nucleus plays a part. Spectrum observations cannot at present decide upon the respective merits of their formulæ.

The constitution of the opium bases.

It is easy to see that the opium bases, morphine, codeïne, and their derivatives, apomorphine-hydrochloride, di-acetyl-codeïne, and tetra-acetyl-morphine, all have a similarly constituted nucleus. This nucleus is a benzene or a pyridene derivative, as shown by the absorption band, extending from about wave-length 3000 to 2600; the effect of alkyl and acetyl substitutions upon the curve of absorption is well exemplified by codeïne, and the acetylated derivatives of codeïne and morphine.

In apomorphine-hydrochloride the intensity of the general absorption is greatly increased, but the position of the band is but little altered, as it lies within wave-lengths above mentioned.

In the greatly increased length of the curve of thebaïne, we have evidence which is not in harmony with the comparatively simple formula $C_{19}H_{21}NO_3$. The substances narceïne, narcotine, and oxynarcotine are all considered to be derivatives of hemipinic acid (WRIGHT and BECKETT, J. Chem. Soc., vol. xxviii., p. 629, and vol. xxix., p. 461), the relationship between the substances being expressed by the following formulæ:—



From these expressions it may be seen that the same benzenoid grouping is common to all, and the narcotine and oxynarcotine stand to each other in the relationship of aldehyde and acid as far as this grouping is concerned.

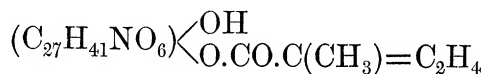
In attempting to trace a connexion between the absorption spectra and the formulæ given above, one is met by a difficulty caused by the large number of oxygen atoms in the molecules, and particularly in those portions which have hitherto yielded no clue to their constitution. The difficulty is due to the fact that carboxyl and COH groups on side-chains, or as forming a portion of the substituted benzene nuclei exhibit great absorptive power. The occurrence of several oxidised radicals may cause the following variations in spectra: (a), the absorption bands become so widened as to extend into the region of rays affected by naphthalene, quinoline, and their derivatives; (b) or the absorption is so powerful that it extends to rays less refrangible than

those in which the band is situated, and continues so far down the curve that the selective absorption is not made manifest. Narcéine appears to be a good example of this; its absorptive power is very great, extending into the region of such low refrangibility as wave-length 3000 when 1 millim. of liquid is examined containing only $\frac{1}{1000}$ of substance, so that no band is visible. In the case of narcotine and oxynarcotine it is difficult to arrive at any conclusion, but, from the extension of their absorption bands, it is probable that the portion of the molecule which has a constitution hitherto undetermined is the principal cause of the absorption. In the case of apomorphine the loss of water appears to cause two molecules of morphine to coalesce, the result being that the band does not suffer displacement to any great extent; it still absorbs rays of approximately the same wave-length, but the band appears far down the curve, or, in other words, the intensity of the absorption, is increased.

The remarks on narcéine are also applicable to papaverine in every particular.

Cevadine.

Cevadine yields on saponification a new base, provisionally called cevine and cevadic or methyl-crotonic acid; its formula therefore as shown by WRIGHT and LUFF (J. Chem. Soc., vol. xxxiii., p. 351) is the following:—



Veratrine.

Veratrine $[(\text{C}_{28}\text{H}_{44}\text{NO}_7) - \text{O.CO.C}_6\text{H}_3(\text{O.CH}_3)_2]$ when saponified decomposes into a new base and di-methyl-protocatechuic acid. Its curve greatly resembles that of codéine and morphine with their derivatives (*ibid.*, p. 355), and is distinctly different in character to that of cevadine, as the latter shows no absorption band. At the present time, however, no inference is to be drawn from this, for we have no knowledge of the constitution of the basic portion of the molecule which is the major part in veratrine.

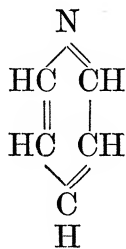
Brucine and Strychnine.

The absorption curves of brucine and strychnine are interesting, the former being essentially different from the latter, as it extends into a much less refrangible portion of the spectrum. It will be observed that the brucine shows two absorption bands, the second, however, is very like that of strychnine, so much so indeed as to cast suspicion upon the purity of the specimen of brucine examined. This, however, cannot be questioned. (See pp. 519–520.)

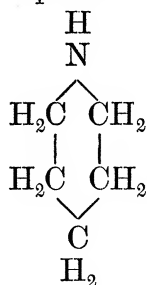
The constitution of piperine.

According to researches of A. W. HOFMANN (Berl. Berichte, vol. 12, p. 984) and of KÆNIGS (*idem*, p. 2341) piperine has a constitution somewhat similar to that of atropine, that is to say, it is a derivative of a hydrogenised pyridine and of piperic acid, which is a benzene derivative, thus:—

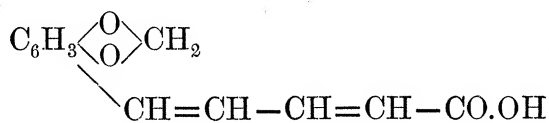
Pyridine.



Piperidine.

Piperidine . . . $\text{C}_5\text{H}_{10}\cdot\text{NH}$ Piperic acid . . . $\text{C}_{12}\text{H}_{10}\text{O}_4$ Piperine . . . $\text{C}_{17}\text{H}_{19}\text{NO}_3$

Piperic acid has the structure represented by FITTIG in the following manner:—



Unlike atropine, piperine shows a very powerful absorption and a persistent absorption band extending from wave-length 3600 to 2740.

The constitution of nicotine.

According to WISCHNEGRADSKY (Ber. 13, p. 2315, 1880), nicotine is an alkyl derivative of a di-hydro-pyridine in which the hydrogen united to the nitrogen is replaced by ethyl, and the second hydrogen is replaced by allyl, thus:— $\text{C}_5\text{H}_4 \left\{ \begin{array}{l} \text{C}_3\text{H}_5 \\ \text{NC}_2\text{H}_5 \end{array} \right.$

The spectrum is quite in accordance with such a constitution, as it yields no absorption bands.

The constitution of atropine.

The constitution of atropine is that of tropine and tropic acid, less a molecule of water, thus:—

 $\text{C}_5\text{H}_7(\text{C}_2\text{H}_4.\text{OH})\text{N}.\text{CH}_3$ Tropine $\text{C}_6\text{H}_5.\text{CH} \left\{ \begin{array}{l} \text{CH}_2.\text{OH} \\ \text{CO.OH} \end{array} \right\}$. Tropic acid $\text{C}_{17}\text{H}_{23}\text{NO}_3$ Atropine

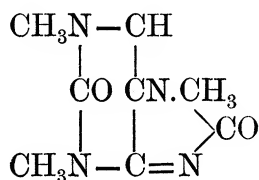
According to LADENBURG tropine is probably an ethylene derivative and a hydro-

genised addition-product of methyl-pyridine. A pyridine nucleus hydrogenised would yield no absorption band and would be very diactinic.

In tropic acid we have a substance capable of manifesting the benzene nucleus by giving a banded spectrum; if however it be modified by hydrogenising, this property disappears. As atropine not only exhibits no absorption band, and is, moreover, a remarkably diactinic substance, it is highly probable that both the pyridine and benzene residues are hydrogenised. (Compare hyoscyamine and piperine.)

Hyoscyamine is isomeric with atropine; on treatment with baryta water it yields tropine and tropic acid. Like atropine it is remarkably diactinic, layers of solutions 20 millims. in thickness, which contained one part of the substance in 200 of alcohol, transmitted all rays in the case of atropine to wave-length 2700, and of hyoscyamine to wave-length 2740.

Caffeine, or *methyltheobromine*, $C_8H_{10}N_4O_2 + H_2O$, has been shown to have the constitution of a tri-methyl-xanthine. According to EMIL FISCHER its structure is represented thus:—



There are no reasons for believing that such a body would yield an absorption band, indeed there is much evidence to lead one to think that it would not. We may therefore say that its supposed constitution is in accordance with its absorption spectrum.

Pyridine, quinoline and derivatives.

The absorption band characteristic of pyridine is strongest between wave-lengths 2700 and 2300, with diminished intensity it extends from 2570 to 2400. It appears highly probable that this substance enters into the constitution of morphia and some other of the opium bases.

As was predicted piperidine shows no absorption band, but still, like the terpenes, it possesses considerable absorptive power, which is exerted on the more refrangible rays, extending continuously to wave-length 2420.

The absorption spectra of two specimens of quinoline yield curves which are precisely similar. The band of absorption is strongest between wave-lengths 3170 and 2600, continuing with diminished intensity it lies between 2980 and 2830. There is in addition a remarkable narrow band of absorption which is very well defined, it lies between 3085 and 3039, and continues with but slightly diminished intensity between 3078 and 3039.

Quinoline hydrochloride yields a spectrum differing from that of the base inasmuch

as it exhibits two absorption bands lying between (1) 3320 and 2740, (2) 2418 and 2199.

Tetra-hydro-quinoline is a more diactinic substance than quinoline, it is characterised by two absorption bands—(1) between 3180 and 2750, and continuing to 2870; (2) between 2700 and 2300, extending further to between 2650 and 2370.

Substances, such as any of the natural alkaloids, which may be derived from di-hydroquinoline or tetra-hydroquinoline, by replacement of the hydrogens by other elements or radicals in such a manner as to have the nucleus of the compound unchanged, must be expected to exhibit absorption bands.

Strychnine.—Strychnine appears to be a derivative of pyridine.

Brucine.—The substance brucine is most probably a derivative of tetra-hydro-quinoline, or an addition product of quinoline of the same character, since there is a remarkable similarity between the curves of the two substances.

I cannot close this paper without acknowledging indebtedness to the great skill and care that my assistant Mr. W. R. BARNETT has bestowed on these later observations.

CONCLUSIONS.

The conclusions to be drawn from this investigation are the following :—

1. The absorption spectra offer a ready and valuable means of ascertaining the purity of preparations of the alkaloids and particularly of establishing their identity. The quantity of some of the alkaloids present in a solution may be estimated by means of the absorption curves. The difference in character of the various specimens known as aconitines may be recognised; thus the comparatively harmless base known as foreign aconitine may be distinguished from those of great physiological activity by its transmission of a continuous spectrum, while the three active specimens of aconitine are distinguished from one another by their characteristic absorption curves.

That each of the three active aconitine bases are substances with a different constitution is a conclusion confirmed by optical examination.

The purity of quinine and absence of any admixture of cinchonine can be readily determined, by reason of the latter substance being much less diactinic than the former, but for the same reason quinine cannot be directly estimated in a mixture of the two bodies.

Drugs of such potency as aconitine, morphine, quinine, strychnine, &c., which ought to be prescribed only when of absolute purity, should be submitted to spectroscopic examination, so that their exact nature and degree of purity may be guaranteed.

2. In comparing the spectra of substances of similar constitution it is observed that such as are derived from bases by the substitution of an alkyl radical for hydrogen, or of an acid radical for hydroxyl, the curve is not altered in character, but may vary in length when equal weights are examined.

This is explained by the absorption bands being caused by the compactness of structure of the nucleus of the molecule, and that equal weights are not molecular weights, so that by substituting the hydrogens of the nucleus by radicals which exert no selective absorption, the result is a reduction in the absorptive power of a given weight of the substance. Examples are afforded by morphine and codëine (methyl-morphine), diacetyl-codëine and tetra-acetyl morphine.

3. Bases which contain oxydised radicals, as hydroxyl, methoxyl, and carboxyl, increase in absorptive power in proportion to the amount of oxygen they contain. This is exemplified by papaverine, narcëine, narcotine, and oxynarcotine. The apo-derivatives are less diactinic than the parent bases. Examples are apo-morphine and pseudaconitine.

Aconitine.

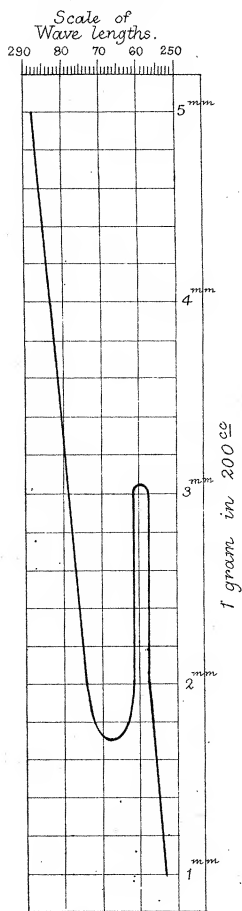


Fig. 1.

English Aconitine

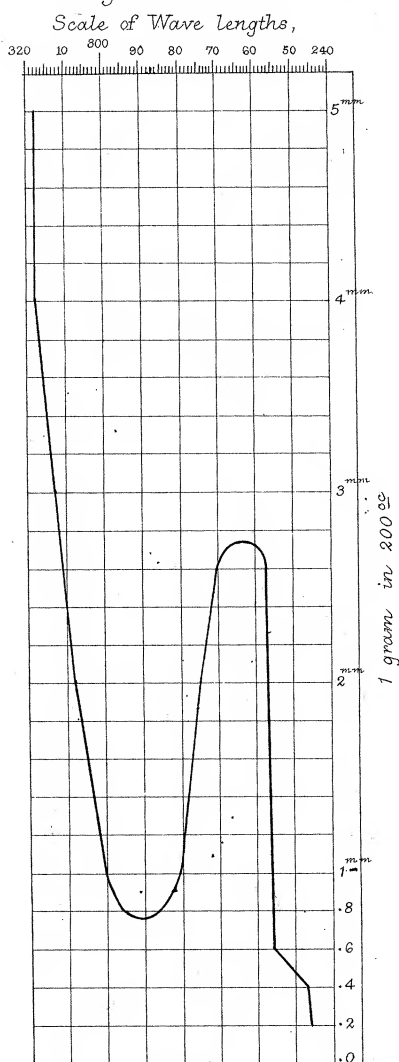


Fig. 2.

Japaconitine

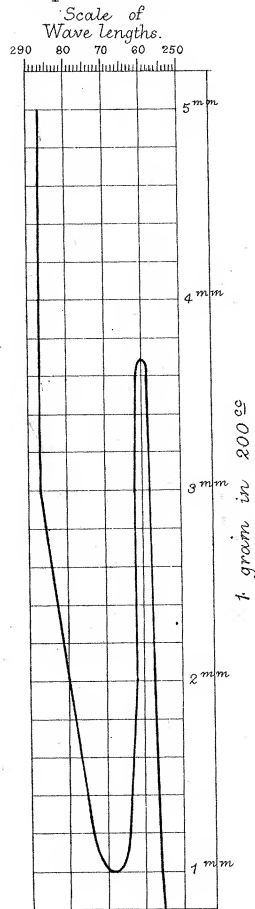


Fig. 3.

Pseudaconitine.

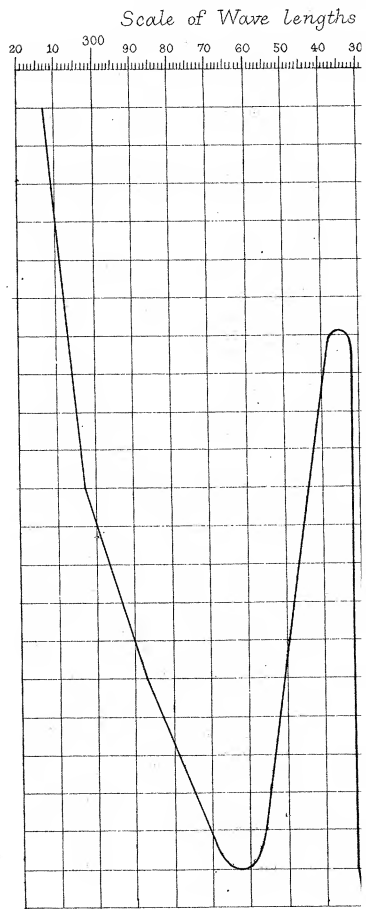
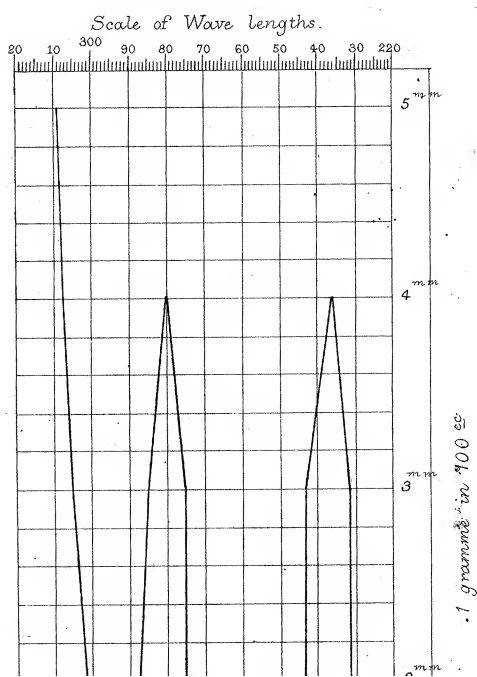
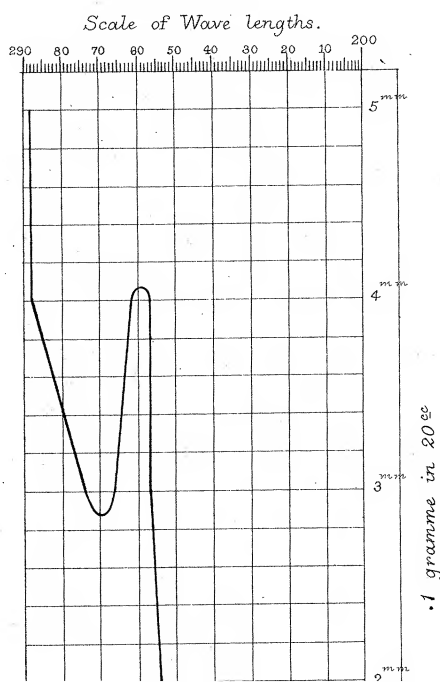


Fig. 4.

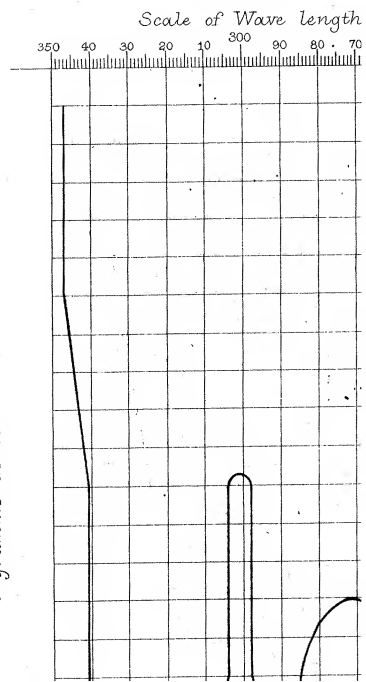
Aconitine



Aconitine



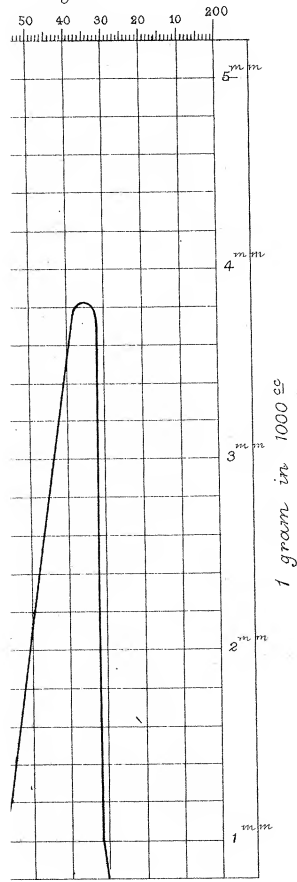
Quinine



385. Plate 53.

nitine.

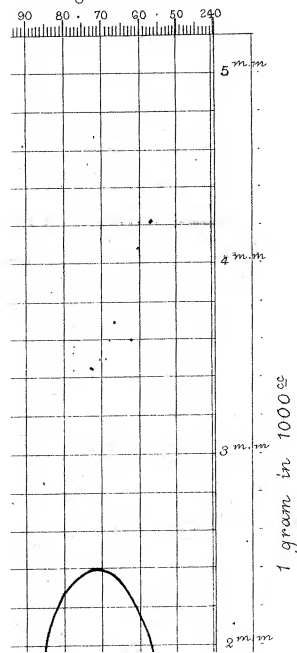
lengths.



4.

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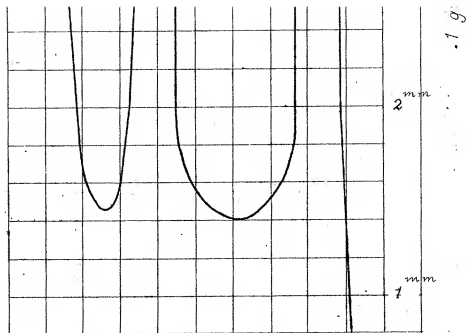


Fig. 5.

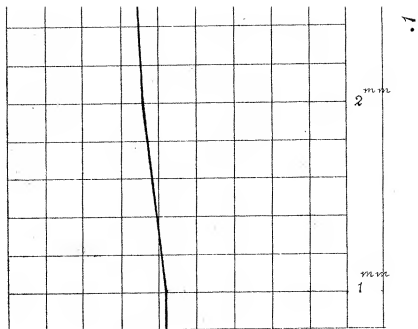


Fig. 6.

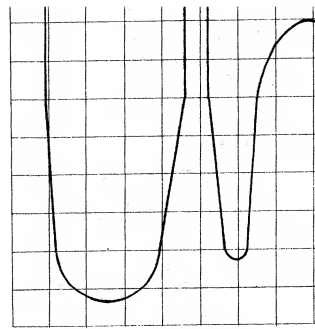
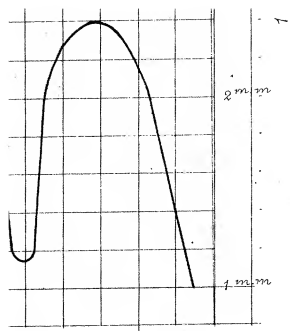


Fig. 7.



. 7.

West Newman & C^o sc.

Quinine Sulphate

Scale of Wave lengths.

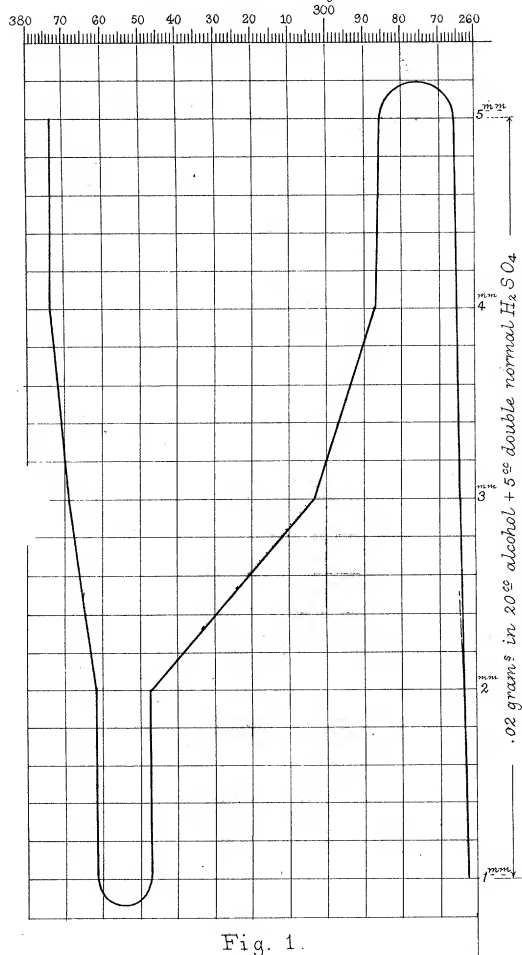


Fig. 1.

Cinchonine,

Scale of Wave lengths.

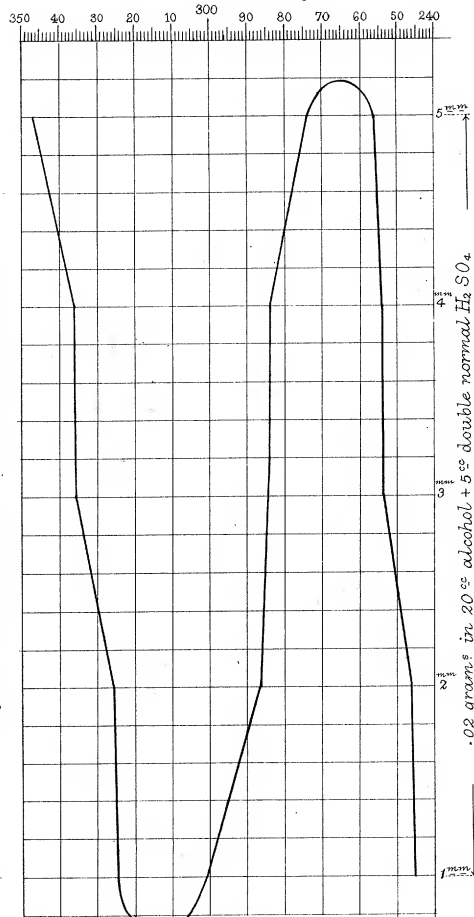


Fig. 2.

Quinidine Sulphate

Scale of Wave lengths.

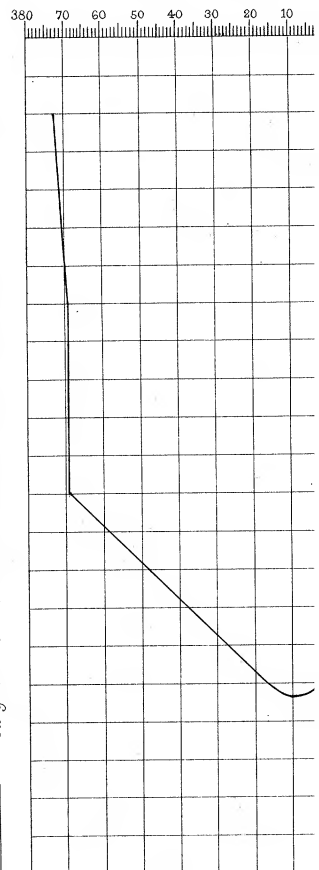
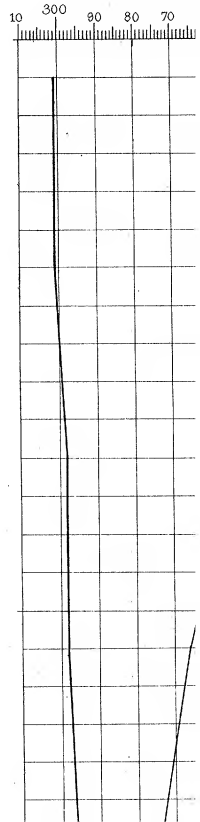


Fig. 3.

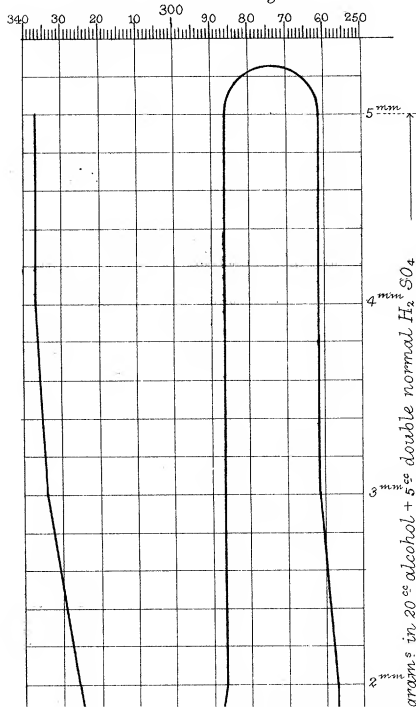
Morphine

Scale of Wave lengths.



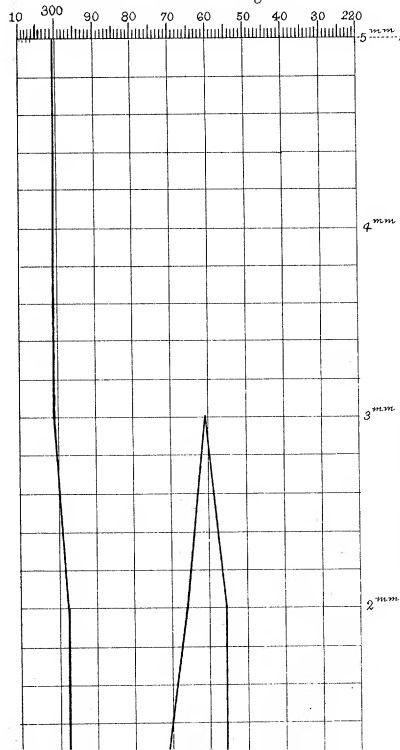
Cinchonidine Sulphate

Scale of Wave lengths.



Morphine

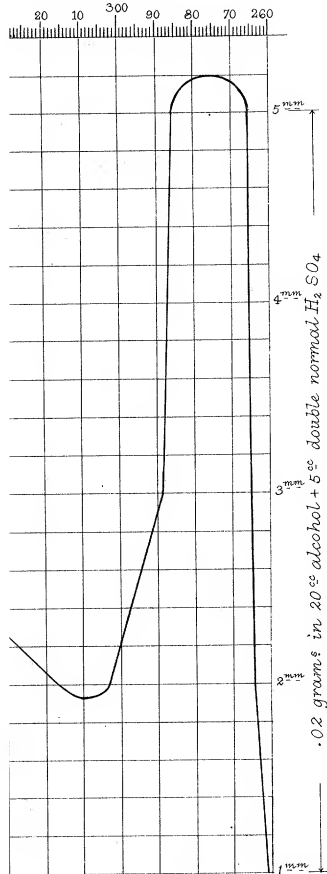
Scale of Wave lengths.



885. Plate 54.

ie Sulphate.

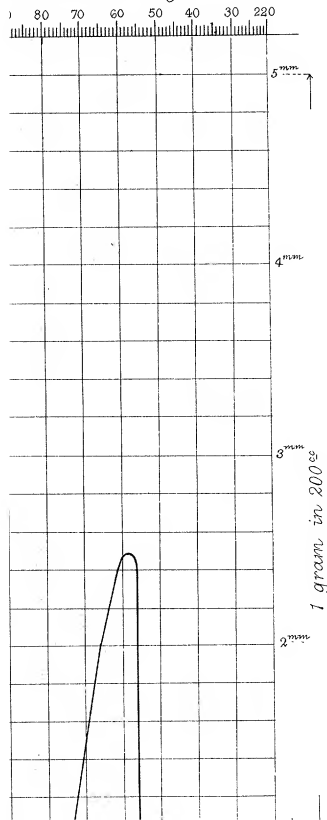
Wave lengths.



3.

Morphine.

ile of Wave lengths.



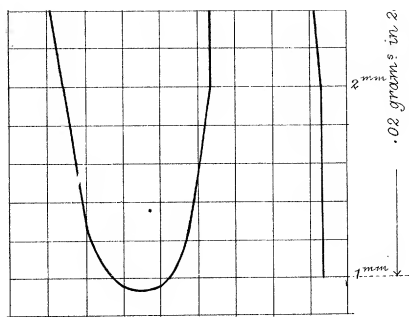


Fig. 4.

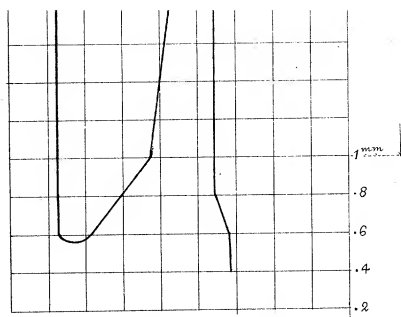


Fig. 5.

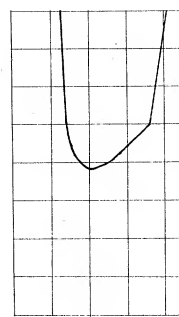


Fig. 6.

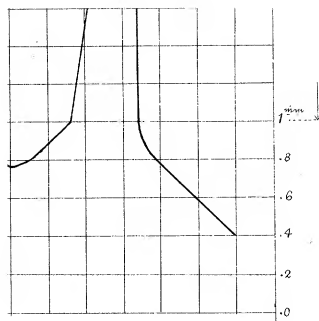


Fig. 6. West, Newman & Co. sc.

Tetracetyl Morphine

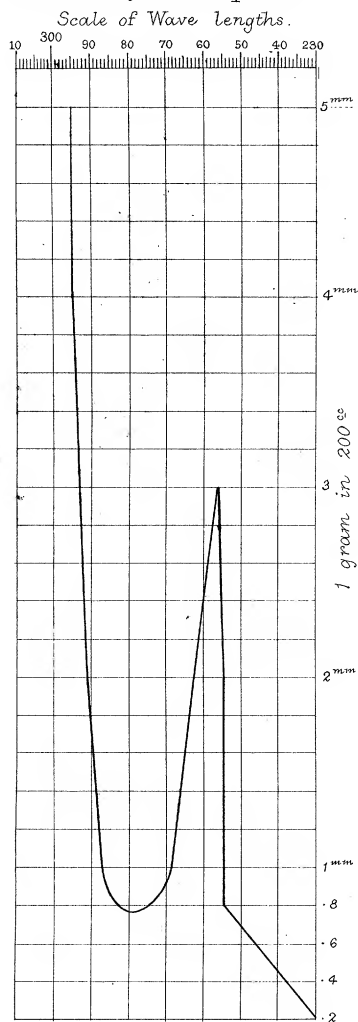


Fig. 1.

Codeine (1)

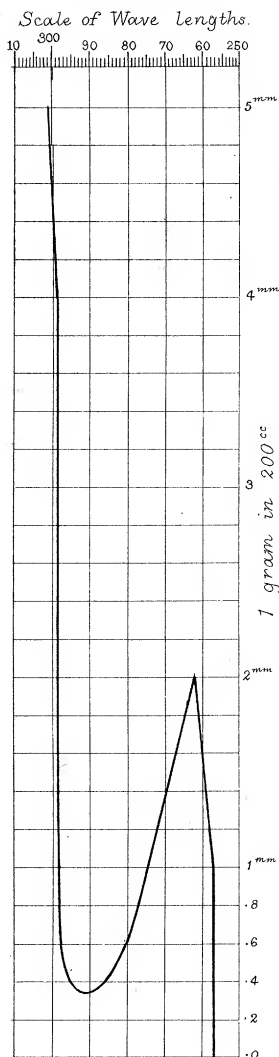


Fig. 2.

Codeine (2)

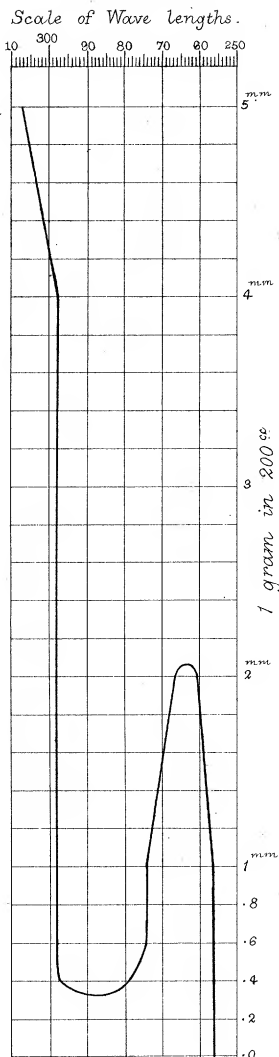


Fig. 3.

Diacetyl Cod

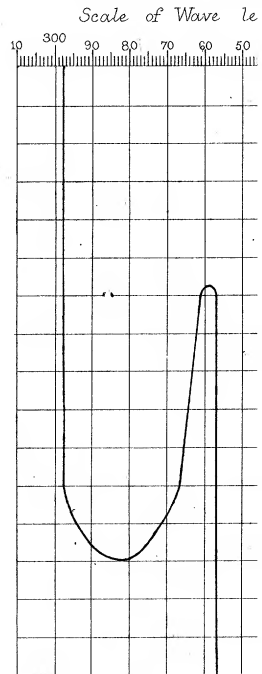
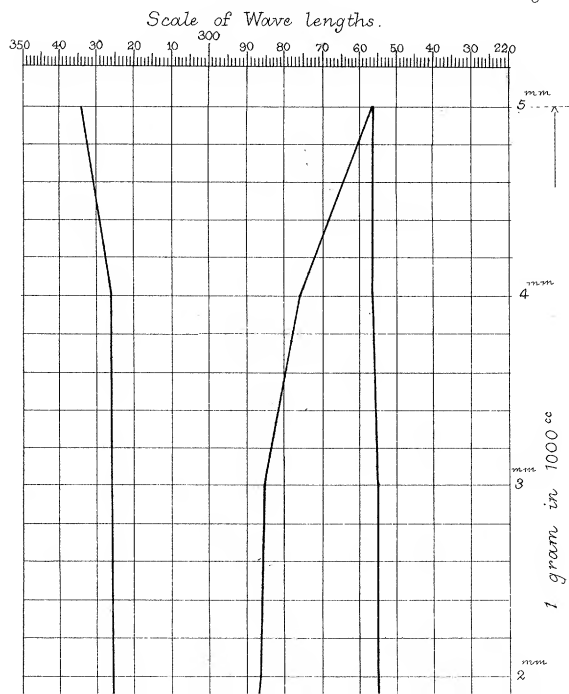
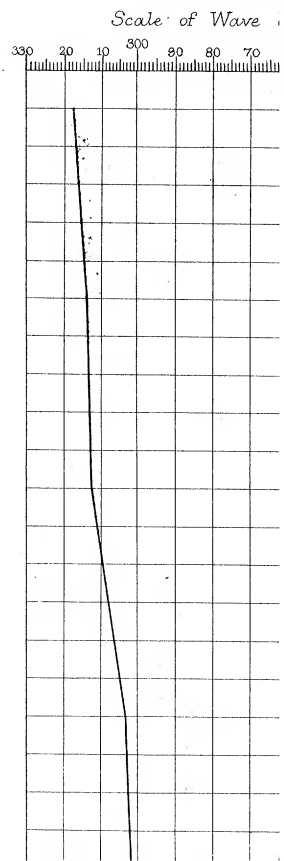


Fig. 4.

Narcotine.



Thebain



tyl Codeine.

Wave lengths.

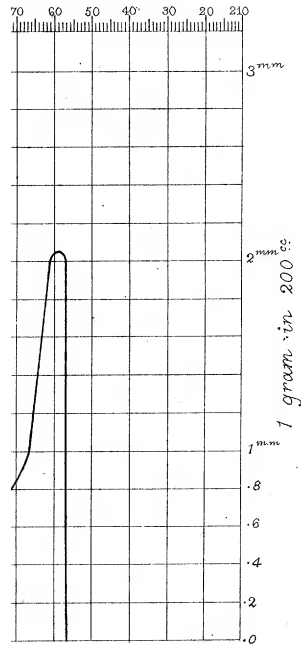
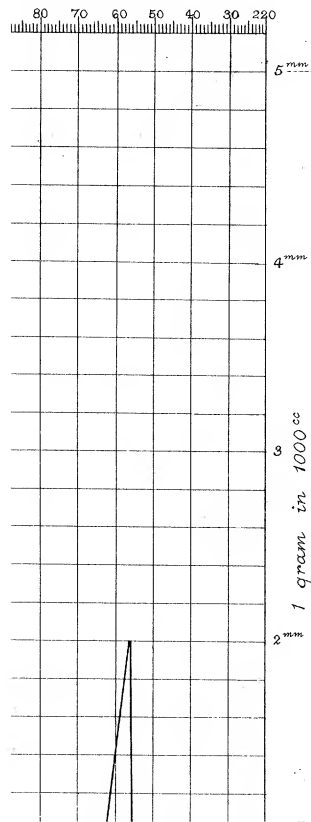


Fig. 4.

hebaïne.

Wave lengths.



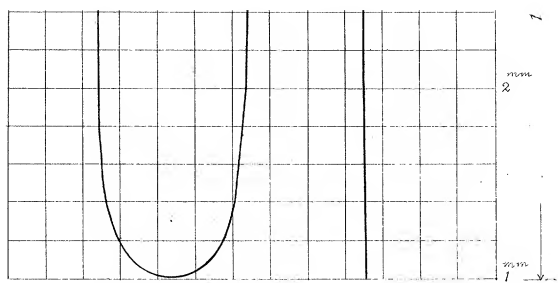


Fig. 6.

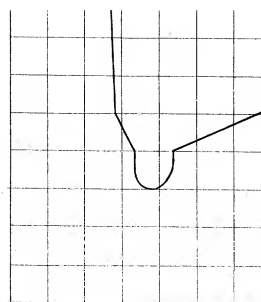


Fig. 5.

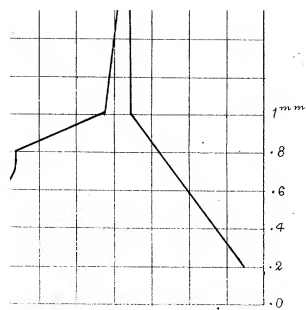
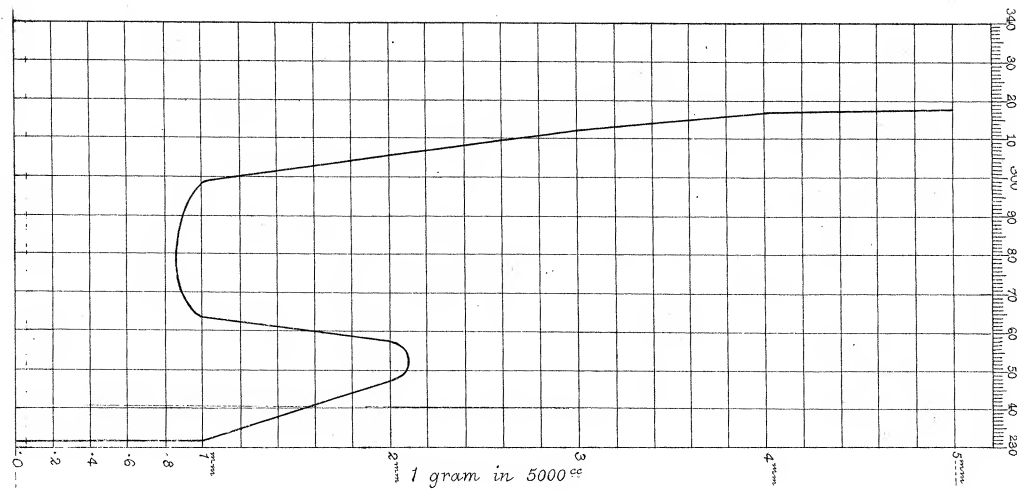


Fig. 5.

West Newman & Co. se.

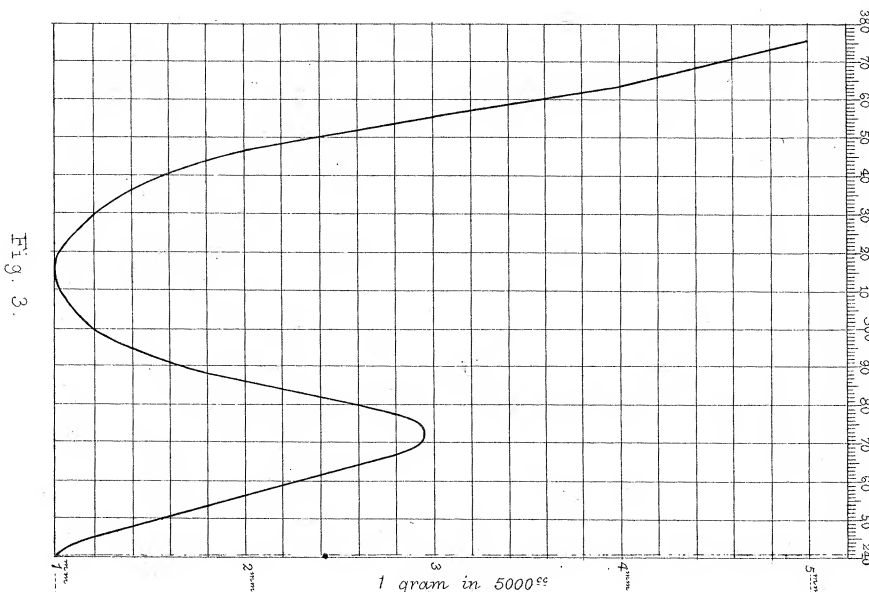
Apomorphine Hydrochloride.

Scale of Wave lengths



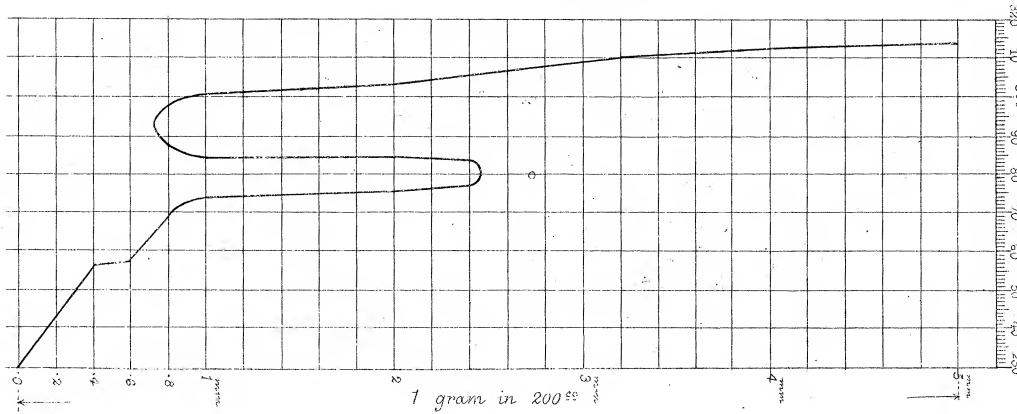
Piperine.

Scale of Wave lengths.



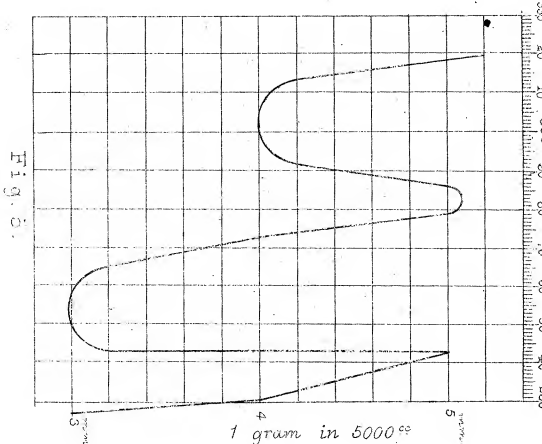
Veratrine

Scale of Wave lengths.



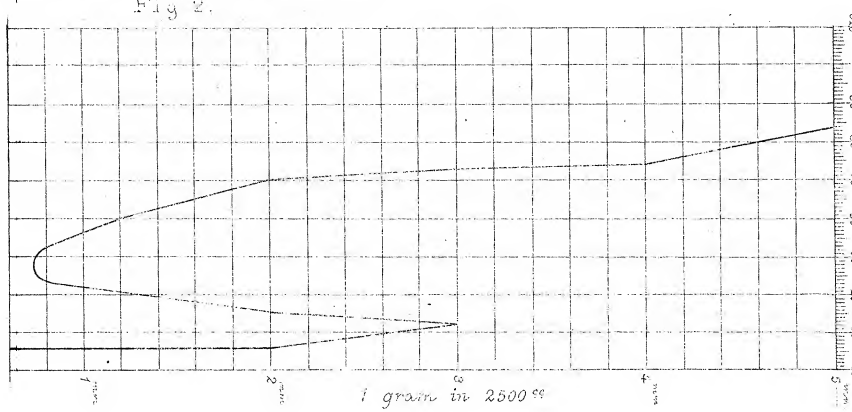
Brucine.

Scale of Wave lengths.



Strychnine.

Scale of Wave lengths.



Oxynarcotine.

Scale of Wave lengths.

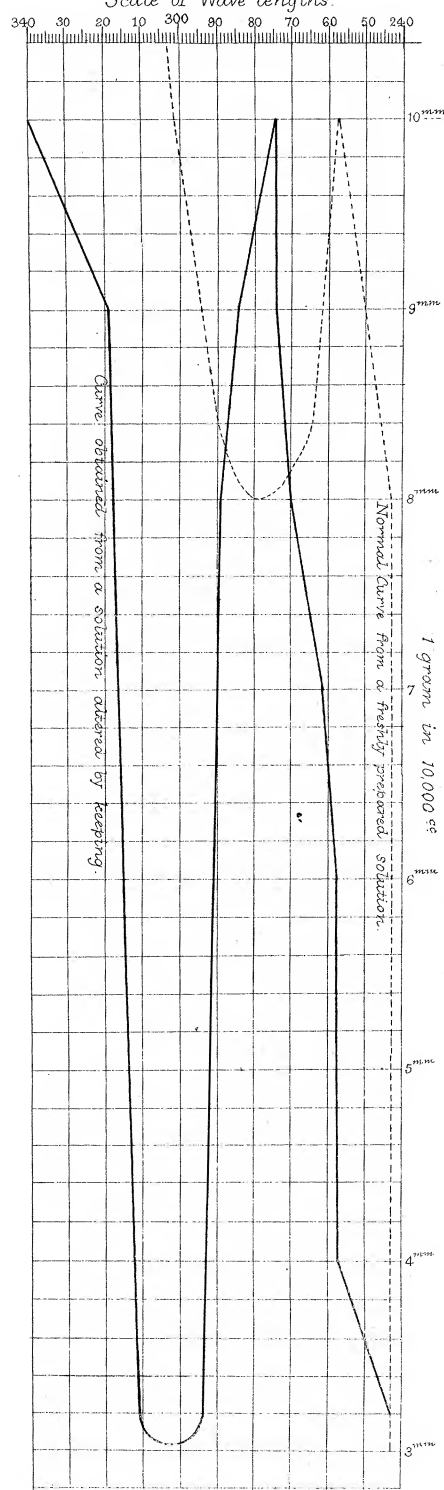




Fig. 1

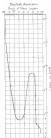


Fig. 2



Fig. 3

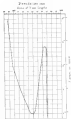


Fig. 4

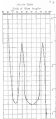


Fig. 5

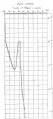


Fig. 6

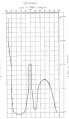


Fig. 7

Quadrant Polygons
Side of base length

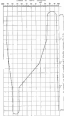


Fig. 1

Quadrant Polygons
Side of base length

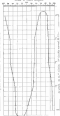


Fig. 2

Quadrant Polygons
Side of base length

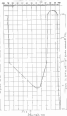


Fig. 3

Quadrant Polygons
Side of base length

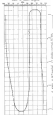


Fig. 4

Quadrant Polygons
Side of base length



Fig. 5

Quadrant Polygons
Side of base length

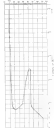


Fig. 6

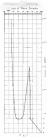


Fig. 1

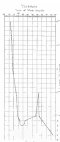
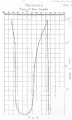


Fig. 2